T.C.
ISTANBUL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES IN
SCIENCE AND ENGINEERING

M. Sc. THESIS

SYNTHESIS AND CHARACTERIZATION OF MULTICOMPONENT

NANOMATERIALS

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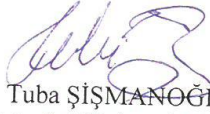**Examamining Committe Members**

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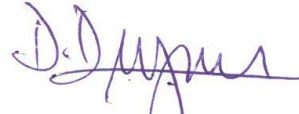Istanbul University
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FOREWORD

This thesis was focused on synthesis and characterization of some nano-metallic oxides. At first, an introduction was given about the field of nanotechnology which discussed about its applications, history of nanomaterials and nanotechnology and different ways of synthesizing nanoparticles. In the experimental aspects, single, binary and composite nano-metallic oxides were prepared and characterized.

Gratitude is to God creator of the heavens and the earth and Lord of what is beneath them. It is He we worship and to Him we must all return. I thank God for given me the opportunity from the start of this work to its fruition.

It is my pleasure at this moment to pronounce my gratitude to my advisor Prof. Dr. Gülin Selda POZAN SOYLU who has being a mentor without hesitation or restriction at any time throughout this work. Her consultancy and the guidance received have made this work came into existence.

December 2017   Bilal Ibrahim DAN-IYA

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Explanation
SnO_2	: Tin (IV) oxide
Bi_2O_3	: Bismuth (III) oxide
TiO_2	: Titanium (IV) oxide
ZrO_2	: Zirconium (IV) oxide
ZnO	: Zinc oxide
$BiOCl$	: Bismuth oxychloride
CO_2	: Carbon (IV) oxide
NH_4OH	: Ammonium Hydroxide
NH_3	: Ammonia Solution
$SnCl_2.2H_2O$	: Tin (II) Chloride Dihydrate
$TiCl_4$	: Titanium Tetrachloride
$NaOH$	: Sodium Hydroxide
HCl	: Hydrochloric Acid
$Bi(CH_3COO)_3$	: Bismuth Triacetate
$Bi(NO_3)_2$	: Bismuth Trinitrate
$Zn(NO_3)_2.6H_2O$	: Zinc trinitrate hexahydrate

Abbreviation	Explanation
AFM	**:** Atomic Force Microscopy
BET	**:** Brunauer, Emmett and Teller
CNTs	**:** Carbon Nanotubes
CVC	**:** Chemical Vapor Condensation
CVD	**:** Chemical Vapor Deposition
EN	**:** Engineered Nanomaterials
FT-IR	**:** Fourier Transform Infrared Spectroscopy
GTL	**:** Gas-to-Liquids
HPPD	**:** Hypersonic Plasma Particle Deposition
HRSEM-EDS	**:** High resolution scanning electron microscopy-electron diffraction spectroscopy
LED	**:** Light Emitting Diodes
LNG	**:** Liquified Natural Gas

MBE   : Molecular Beam Epitaxy
SEM   : Scanning Electron Microscopy
SPMs   : Scanning Probe Microscopes
STM   : Scanning Tunneling microscope
TEM   : Transmission Electron Microscopy
TEOS   : Tetraethoxysilanes
TMOS   : Tetramethoxysilane
UHV   : Ultra High Vacuum
XPS   : X-Ray photoelectron spectroscopy
XRD   : X-Ray Diffraction

ÖZET

YÜKSEK LİSANS TEZİ

Bilal Ibrahim DAN-IYA

ÇOK BILEŞENLI NANOMALZEMELERIN HAZIRLANMASI VE KARAKTERIZASYONU

İstanbul Üniversitesi

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Biyo ve Nano Teknolojisi Mühendisliği Anabilim Dalı

Danışman: Prof. Dr. Gülin Selda POZAN SOYLU

Nano teknolojinin tanımı, uygulama alanları ve yararları, nano materyallerin tanımı, özellikleri ve üretim metotları hakkındaki açıklamalar tezde sunulmuştur. Ayrıca, literatürdeki çalışmalar dikkate alınarak, nano-metal oksitler ve uygulama alanları da incelenmiştir. Bu tez çalışmasında, saf kalay (IV) oksit (SnO_2), titanyum (IV) oksit (TiO_2), zirkonyum (IV) oksit (ZrO_2), bizmut (III) oksit (Bi_2O_3) ve çinko oksit (ZnO) sol-gel ve birlikte çöktürme metotları kullanılarak hazırlanmıştır. Ayrıca, TiO_2-Bi_2O_3, ZnO-Bi_2O_3 ve ZrO_2-Bi_2O_3 ikili oksitleri katı hal metodu ile hazırlanmıştır. Buna ilaveten, basit sol-gel metod ile kristal yapıda saf bizmut oksiklorür (BiOCl) nano-kompozit sentezlenmiştir. Numunelerin yapı, morfoloji ve bant değerleri, sırasıyla X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM) ve Fourier dönüşümlü kızılötesi spektroskopisi (FT-IR) ile tanımlanmıştır. Karakterizasyon sonrası, sırasıyla SnO_2, Bi_2O_3, TiO_2, ZnO ve ZrO_2 için tetragonal, monoklinik, anataz, heksagonal ve tetragonal fazı doğrulanmıştır. Monoklinik α-Bi_2O_3, tüm ikili oksit numunelerde doğrulanmıştır. Bununla birlikte, saf anataz faz TiO_2, tetragonal faz ZrO_2 ve heksagonal faz ZnO sırasıyla TiO_2-Bi_2O_3, ZrO_2-Bi_2O_3 ve ZnO-Bi_2O_3 ikili oksitlerde doğrulanmıştır ve ikili metal oksit nanokompozitlerdeki metal oksit kristal boyutlarının değiştiği gözlenmiştir.

Aralık 2017, 83 sayfa.

Anahtar kelimeler: Nanoteknoloji, Nanokompozit, İkili oksit.

SUMMARY

M.Sc. THESIS

SYNTHESIS AND CHARACTERIZATION OF MULTICOMPONENT NANOMATERIALS

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In this study, sol-gel and co-precipitation methods were used to synthesize pure tin (IV) oxide (SnO_2), titanium (IV) oxide (TiO_2), zirconium (IV) oxide (ZrO_2), bismuth (III) oxide (Bi_2O_3) and zinc oxide (ZnO). Moreover, binary oxides of TiO_2-Bi_2O_3, ZnO-Bi_2O_3 and ZrO_2-Bi_2O_3 were prepared by solid state method. In addition, pure and crystalline Bismuth oxychloride (BiOCl) nanocomposite was also synthesized with simple sol-gel method. The structure, morphology and bands of samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FT-IR) respectively. After characterizations, a tetragonal, monoclinic, anatase, hexagonal and tetragonal phase of SnO_2, Bi_2O_3, TiO_2, ZnO and ZrO_2 were confirmed respectively. Monoclinic α-Bi_2O_3 was confirmed in all binary oxides samples, however, pure anatase phase TiO_2, tetragonal phase ZrO_2 and hexagonal phase ZnO confirmed in TiO_2- Bi_2O_3, ZrO_2- Bi_2O_3 and ZnO- Bi_2O_3 binary oxides respectively and also it was observed that there were changes in crystalline sizes of metallic oxides in binary oxide nanocomposites.

December 2017, 83 pages.

Keywords: Nanotechnology, Nanocomposite, Binary oxides

1. INTRODUCTION

1.1 Definition of Nanotechnology

Nanotechnology is an aspect of science and technology that deals with alteration and modification of materials at the nanometer scale usually from 1 to 100 nm – (Fig. 1), in the nanometer scale, constituents are categorized based on variation of their different properties instead of their dimensions equivalence. Nanotechnology is an area that is considered to be the "Platform technology" due to the fact that it can merge together with other technological aspects usually based on scientific concepts (March and Schmidt, 2007). Nanotechnology is emerging as a new technology involving different academic areas such as material science, medicine, biology, chemistry and physics. The prefix "nano" in the term nanotechnology was derived from a Greek word *nanos*, which means "*dwarf*" and which relates to one billionth (10^{-9} m) in size or at least one of a dimension of any engineered material, thus considered to be in nanometer (nm). It can also mean the length of approximately three atoms that are close or next to one another. In contrast however, the DNA molecule is considered to be 2.5 nm wide, where as a protein, flu virus and the human hair were considered to be about 50 nm, 100 nm and 10,000 nm thick respectively (Fig.2&4). Due to the ease with which they can be produced in various shapes, nanomaterials are thus interesting nanoscale systems. These interesting materials could be the answer to the anticipating science dreams to be achieved in the near future (Hulkoti and Taranath, 2014).
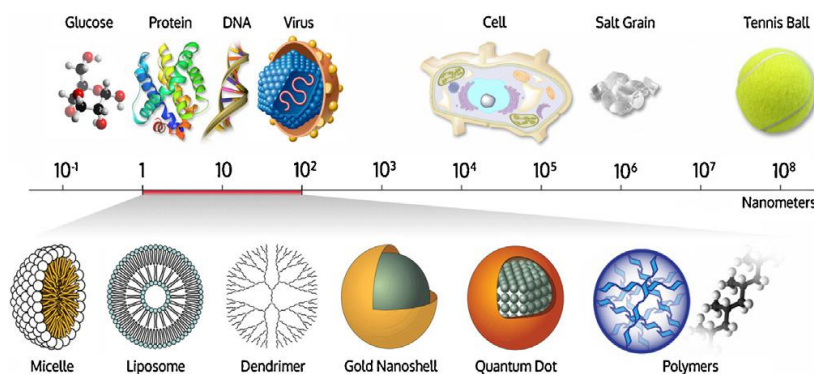
Figure 1.1: Materials at nanometer by Richard Feynman.
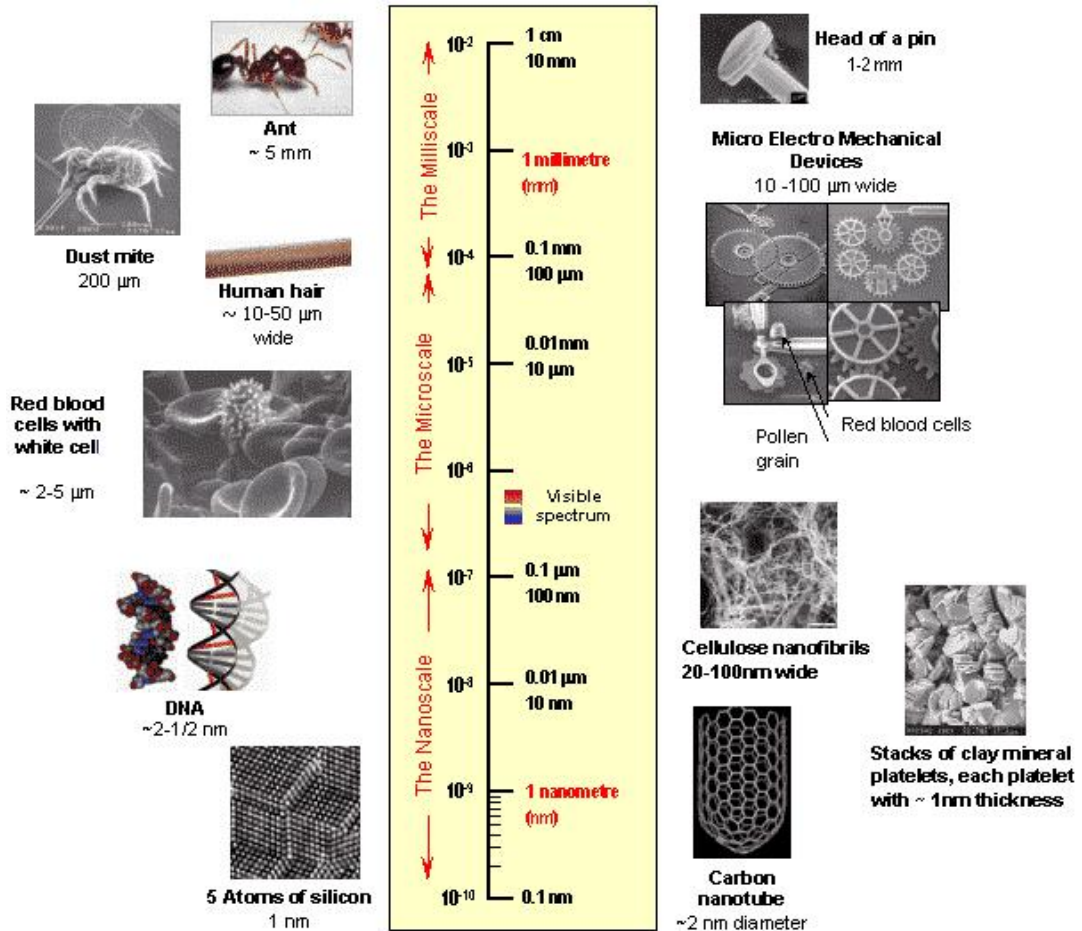
Figure 1.2: Different sizes of materials scaling in nanometers, micrometers and millimeters.

1.2 Nanotechnology History

In nature and ever since the beginning of the earth, nanotechnology has been in occurrence through mutation, adaptation and evolution. By this process and via the help of very small conformations namely "chloroplast" that exist in nanometer, plants passed through a photosynthetic route. Moreover, one more usual occurrence is in the field of bioscience using enzymes otherwise chemical catalysis using catalysts involving in catalyzing a particular chemical or biochemical reaction (Smith, 1997). James Clerk Maxwell 1867 was the first man to carry out an investigation on a molecule utilizing nano range. The foremost to categorize constituents in dimensions on nano level base was Zsigmondy in 1914, from which advances were being made in characterization in particulate sizes by Blodgett and Langmuir in 1920s through introduction of monolayer. Measurement of surface force was also first reported by Derjaguin (1954).

Nanotechnology was first learned from Richard Feynman in 1959 (Fig.1) from his popular speech, titled "There is plenty of room at the bottom" hosted by the American Institute of Technology. He proposed a technique using some specific tools for the manipulation of atoms and molecules (Gribbin, 1997). With various improvements, nanotechnology was proposed to be defined by Taniguchi (1974) (Fig.3) as a method that involves manipulating matter at the nanoscale which involves processing, separating, consolidating and deforming of molecules of interest. Among the tools used in the 1980s were atomic force microscopy (AFM), scanning tunneling microscope (STM), molecular beam epitaxy (MBE) and scanning probe microscopes (SPMs). As a result of latest development in skills and knowhow, new methodical apparatuses are now in use to determine, morphological and surface structure, quantify the phase composition, basic conformation in addition to crystal dimension of a nano sample. Among these equipments include Atomic force microscopy (AFM), X-ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), high resolution scanning electron microscopy-electron diffraction spectroscopy (HRSEM-EDS) and the list goes on (Bankole et al., 2014)

Figure 1.3: Prof. Norio Taniguchi.   **Figure 1.4:** Different sizes of nanomaterials.

1.3 Applications of Nanotechnology

The significance of the applicability of nanotechnology towards conservational, engineering function and decrease in energy utilization that provides lesser price and in turn improving the making effectiveness can never be overstressed. Although, it may not be a complete way out to today's world's problem but perhaps, this technical knowhow can confidently minimize world's financial trials especially those existing in

the developing countries like Africa to be more specific. Examples of such drawbacks may include; treatment of epidemic diseases, the need for clean water (Fieischer, 2008), various manufacturing purposes and numerous methodical innovations. Presently, governments of European countries, USA China and South Africa are continuing to give precedence to technical knowhow via huge investments in nanotechnology with single goal of strengthening financial improvement. Africa on the other hand, is also in desperate need of such innovative technology (Bankole et al., 2014).

1.3.1 Nanotechnology application for water treatment

The high surface area to volume ratio possessed by nanoparticles which can be controlled chemically present's great potential of nanotechnology; as sorbents, materials which latch on to pollutants and extract them out of solution. Example is multi-walled carbon nanotubes which show a leading position, activated carbon less effective than copper and cadmium, a sorbent that is generally utilized. Other nano dimensioned particles that also act potentially as catalysts may include nanometer iron of zero valency and titania nano dimensioned particulates which can be useful in cutting down intractable organic contaminants into nontoxic substances. An example is nanometer zero valent iron can make organic substances of halogens harmless. Silver and magnesium are example of other bioactive nanoparticles which can destroy microbes and utilized instead to sanitize water in the presence of chlorine (Bankole et al., 2014).

Due to the difficulty of the current technology to trap, pin point and eliminate viruses and other toxins, devices that are used in filtration and nano-manufactured membranes can be applicable (Theron et al., 2008). Such membranes and filtration devices may help in monitoring these pollutants at the manufacturing areas and water sanitizing factories. Nanospores membranes are constructed to simultaneously identify and get rid of those contaminants. Industrial wastewater and also the ocean having great potential to eradicate undesirable materials might come to be obtainable to maximize the source of sanitized water. A promising example among others is nanometer iron of zero valency which is being examined and utilized in getting rid of solvents from driven groundwater. Nano titanium (IV) oxide can remain activated by sunlight when scattered into a polluted water and in turn potentially degrading reasonably a huge amount of organic contaminants like dioxins including PCBs with the help of hydroxyl radicals produced (Bankole et al., 2014).

This technology was assumed responsibly to possess influence on water management starting using sorbents of nanoscale and nano bioactive particles which may be incorporated in a functional refining scheme. Novel types of tools that utilized nanotechnology to enhance the effectiveness of purification, getting rid of additional types of contaminants and roles, like water-purity sensors could eventually replace entirely these first hybrid technologies. Researchers are presently examining considerably certain number of materials that exist at nano level. Novel lesser scale water treatment schemes may include sorbents, catalysts, sensors all of nanoscale and smart membranes, nanosensors and other types of nanotechnological appliances (Bankole et al., 2014).

Unfortunately, despite our challenges towards dealing with longstanding draw backs, novel typed contaminants are being increasingly revealed in water supplies. As such improved nano water separation schemes systems may be established to deal with these pollutants. Nano enhanced technology as applicable to water refining systems is via a material usually known to be *nanomaterial*. There exist materials of this nano range which function in as membrane for purification of water, thus these include carbon nanotubes, metal nanoparticles and many more (Theron et al., 2008). These nanomaterials present new ability detoxify contaminated groundwater, outward water and inner water which may be contaminated by inorganic materials and pathogens.

Nano size materials are incredibly efficient for water detoxification as they have quite amount of properties involved, nanomaterials possess large surface area to volume ratio that happens due to decrease in dimension of adsorbent material from large to the size of a nanometer. This decrease in size of adsorbent particle makes adsorption regarded economically more viable and effective method for purification of water. Nanomaterial's characteristics makes higher number of particles attached themselves to toxins which in turn enhances the adsorption ability of sorbent constituents.

The higher surface zone, dimension and other properties like electronic and catalytic of nanomaterials render compromising chances to make more effective water detoxifying catalysts as well as redox vibrant media that has been gaining consideration recently, for example in UV light detoxification of water photocatalyst like TiO_2. TiO_2 nanoparticle synthesis using sol-gel, precipitation and so on are familiar investigatory techniques. As struggles persists in solving global water pollution problem, TiO_2 which is part of

the heterogeneous photocatalysts was recognized in findings and innovations, apart from that, the method presents less-expensiveness, environmentally welcoming and maintainable in the industry devoid generating harmful sludge. With various chemical groups, these cutting-edge nano particulate materials can also be restrained to elevate their attraction towards particular compound (Bankole et al., 2014).

1.3.2 Nanotechnology application for energy development

Although not accessible, there will be a need to convert the energy existing around us into a usable form. Considering the availability and convenient forms of energy in energy-rich materials, they are also quite less difficult to change into some specific yields, such as articulated energies, and electricity which can be extensively circulated. This technology can function in minimizing losses as renovation of energy precedes there by paving way for an alternative when fossil fuels are being depleted. For example, generation of several products of petroleum as a result of conversion of crude oil could be improved by nano-engineered catalysts, together with coal renovation into spotless fuels for producing electricity. Nanotechnology can be used to maximize opportunities in oil and gas applications, in more precisely to produce geothermal reserves by improving thermal conductivity, down-hole split-up improvement, and production of non-destructive substances which can function in geothermal-energy development could be achieved. Metallic nanomaterials may be utilized in geochemical exploration by delineating ore deposits. This technology could also be used in improving the drilling processes. In justification to that, enhanced fluid that is coupled with nano particulate matter and fine powder which importantly improves penetrating speed has been developed by some specialized petroleum laboratories. This blend makes it possible to extract more oil by extinguishing or eliminating destruction to the reservoir well (Esmaeili, 2009).

Additionally, enhancement of the unconventional and stranded gas resources is an application of nanotechnology. The efficiency and infrastructure of liquefied-natural-gas (LNG), LNG quality, and developing gas-to-liquids (GTL) technology are near-term challenges of great focus. In solving the challenges linked with gaining access to stocked natural-gas sources, nanoscale catalysts and nanoscale membranes for GTL produce and nano constituents for compacted-natural-gas conveyance can be developed and created respectively (Esmaeili, 2009).

Novel electrical generating method as another nanotechnology application includes electro-kinetic power generation; this involves fluids with charged ions that create current when enforced via a nano dimensioned pathway. This method mimics the electro-chemical technique in animal neurons (nerve cells) during action potential generation. Despite its non-usage for huge capacities of power generation, this technical knowhow is admirably important in initiating other nano appliances. In energy storage, solar energy assembling and proficiency is enhanced with the increase in surface area to volume ratio of nanoparticles, this improvement is achieved with revealing additional surfaces of conducting feature to the sunlight. The most probably promising alternative energy production is solar cells research and development using nanotechnology (Gardner, 2008).

Solar cells can be more efficient, cheaper and lighter using quantum dots, fullerenes and carbon nanotubes (CNT). For example, amount of light collection can greatly increase by creating photovoltaics with CNTs. Quantum dots that has the potential to captivate several rays of light which give active solar cells are been used by Notre Dame Researchers in the near future. Increase in photovoltaic effectiveness thru the utilization of substances such as lead-selinide is another area that nanotechnology will impact greatly. When a light photon hit these materials, the materials cause more electrons (and therefore more electricity) to be released. Additionally, nanotechnology can be used to modify structural properties of photovoltaics (Bankole et al., 2014).

Photovoltaics that give rise to highly improved solar cells suppleness which has not been featured with several silicon made cells where been able to be constructed from nanowires by the ASTAR Institute of Microelectronics. Energy must be stored and to be used when needed. The application of nanotechnology in the near term could help in creating devices and other products that efficiently store much amount of energy, this implies taking up charge by those appliances or devices and holding it over a time period. Engineered nanomaterials are utilized by many research groups to create better batteries (Schmidt, 2007). Power density to battery size will increase in batteries when they are constructed with nanomaterials, (Gardner, 2008). Battery strength efficiency somewhat rely on dispersion distance and electrolyte polymers of hydrophilic nature and battery efficiency is set to dramatically increase. A prototype battery developed by Altair Technologies which can be charged in six minutes has three times the capacity

existing batteries. The two final issues in lithium-ion batteries are concerns that scientist are presently trying to address. In that regard, they have invented batteries that do not allow electrode contact before battery activation. As opposed to two years, it renders the resultant produce active of 25 years and an approximately limitless shelf life (Bankole et al., 2014).

In addition, normally toxic outputs from typical batteries are neutralized by chemicals released by reserve cells within the batteries during disposal (Baxter et al., 2009). Application of nanotechnology could revolutionize hybrid car industry in battery production. Powered by Altair-Nano lithium ion Nano-safe battery, Micro-Vett Fiat Doblo had journeyed 186 miles amid charging (<10 min). Five hundred nano-enhanced sporting value automobiles in an estimation will be selling in future by phoenix motors and to be featured by Altair technology. The use of viruses to self-gather battery constituents and "printable" sheets of batteries produced from CNTs are concerning fields being investigated to improve battery technical knowhow (Gardner, 2008).

Similarly, this technology will provide impressing improvements in hydrogen energy production, distribution as well as storage. Related techniques to photovoltaics are applied in hydrogen production systems. Hydrogen production that involves separating molecule of water by light can eliminate reliance on remnant fuels. Thus, the technique needs accuracy, and presently, examination into this development process exists at infancy. Among the greatest interesting fields where nanoscale knowledge will influence greatly to hydrogen power is its effective storing. Currently, there exist non-reliable knowhow to preserve huge amount of hydrogen due to the fact that it is either expensive or too large to be stored, as such this justifies the role of nanotechnology as another way of generating energy in this regard.

Exceptionally slim, even and with elevated surface area "nano blades" possess being developed by researchers at Rensselaer. Furthermore, researchers have discovered fullerenes was able to retain huge quantity of hydrogen which is equal to its (hydrogen) density in Jupiter. Presently, pipelines are used, however, the use of carbon nanotubes wiring could greatly further improve the efficiency of hydrogen transport instead of the pipelines. There will be an increase in power, steadiness and conductivity of these lines when there is rise in temperature. Scientists are studying carbon nanotube connection solely to serve that need. İn addition, New Mexico Tech created nanoparticles monitors

to detect potential impurities when placed in hydrogen transport pathways (Gardner, 2008).

Moreover, it could also serve in developing novel types of materials of good conducting property for efficient energy transmission; these materials lose a very little amount of power when electricity travels below. Findings and investigation has been ongoing by many research groups to discover whether nano coatings and nanowires could reduce losses in electrical-transmission lines. The application of nano-science may result to inventions that will deviously safeguard huge quantities of remnant energies for efficient energy utilization. Nanomanufacturing may also pave way in creating entire materials types while utilizing little amount of energy. Considering nano sized sensors as an example, may be utilized to reduce waste and to detect the kind of energy used (Schmidt, 2007).

1.3.3 Nanomedicine applications

Nanomedicine Assist in fore sighting main illnesses which could be suspected to manifest in an individual's body system. The aim is to thorough fully examine with accuracy numerous of several constituents in an individual's body to determine disease risks. Hence, will there by help in understanding the overall individual's state of health. Many researchers are working on creating a "labon-a-chip" device using nanoscale knowledge to perform detailed analysis of a drop of blood. This discovery would notify the doctor to early precursors of disease that reveal both genetic tendencies and environmental factors, such as exposure to air pollution, diet, exercise and stress. Preventive treatment concentrates on timely involvement. With its help, patients are prevented from the total manifestation of diseases and manage it efficiently over time. Nano based knowledge assist in improving growth of profound investigative tests, together with disease management and fitness controlling devices.

Diabetes management among major areas will be at an advantage, early stages of insulin resistance could be detected by Nano based diagnostic tests. Equally, preventive medicine may of significance in dealing with heart dysfunction and hypertension efficiently that affects large portion of a population. Such method can be enhanced to be applied in controlling several illnesses, e.g. arthritis as well as lupus. Equally, personal medication's dream was that a person's information could be utilized in

observing and controlling the medication. The physician's effective medical strategy could be much greater if perhaps has an idea on a particular individual's illness type, metabolic information about drugs, hepatic condition and other illnesses risks. Nanoengineering can make available novel apparatuses required in assembling comprehensive figures on statuses of disease changes and on distinctive factors of management. Significantly, this technology could outgrow the personal medication uprising through facilitating actual, thoughtful control of drug treatment. By providing recurrent response, the physician can without difficulties modify medicines and prescriptions for a person's treatment.

On the other hand, in contributory (reformative) medication, the anticipation concerning possibility for reformative medication largely concentrated upon stem cells. In addition, nano based technology can additionally result to profoundly novel therapy that will deal with spinal injuries, Type 1 diabetes, macular deterioration and other medical problems. The aim, regarding all these instances, was to normalize a section of a person's body from injuries owing to disease, normal aging or genetic malfunctions. Perhaps, researchers may focus on stem cells ability to regenerate tissues and reconstruct function, nevertheless a similarly hopeful method is to engage artificial tissues of nanoscale based. Nonetheless, it is stagnant premature several test centers are investigating coupled with extensive materials scaffoldings which could make cells to produce synthetic tissues, example; liver or bone. Inoculating nanomaterials with to damage nerves seems to be a promising method of making channeling structures. Some nano manufactured structures demonstrate potentially bases aimed at developing 3-D complexes of blood vessels. Moreover, redeveloping dead cells is another tactic and missing role that might also be reestablished by means of Nano-enhanced replacement parts for the body devices that hook into the nervous system (Bankole et al., 2014).

1.3.4 Other applications of nanotechnology

Apart from the three most vital applications of nanotechnology talked over above, it has been proven to be beneficial and useful in various other areas. Nano-technological advances are on the loose in diverse means to affirmative effects on the protection of resources and environment. For example, newly available nano sized catalysts are the bases for alternative reaction paths in the chemical industry, it preserved at lower temperatures additional energy as well as the low amounts of by-products justifying its

selectivity, allow optimal material usage. As naturally pleasant materials, entirely novel starting constituent resources, example is novel bioplastics, possessed the potentiality in substituting conservative polymers and equally metals, for instance car construction. They are categorized via virtually neutral CO_2 stability and made of renewables, and also lead to an increase in liberation starting with petroleum centered initial constituents. It was known that CNT acts progressively significant function towards enhancing novel constituents.

Literature also make known that the idea of nanotechnology can be useful in the advancement of conservational defensive constituents, nano scaled substance for brilliant highway, stab or bullet-proof nanoscale material, low friction material and detection of fabricating materials. Additionally, application fields of nano based technical knowhow can be; agriculture as well as nutrition, electronics, communication, etc.

1.4 Nanotechnological Paybacks

Paybacks of nano based technology aimed at maintainable advancement are enormous, however, briefed below:

   i.   Price effectual utilization of renewable power
   ii.   Timely conservational management and remediation
   iii.   Less energy needed and waste productions strategies
   iv.   Simpler and powerful nano based substance
   v.   Timely illness identifiers aimed at protective medication
   vi.   Lesser, precise and thoughtful detecting and checking tools.

1.5 What are Nanomaterials?

Nanoscale materials are constituents in which the tiniest size exists approximately below 100 nm. A nanometer is approximately 100,000 times smaller than the diameter of a human hair – one millionth of a millimeter. Nanomaterials are of concern due to the fact that in this dimension distinctive properties appear. Such evolving features possess the capacity of countless effects in medicine, microelectronics and some other fields (Alagarasi, 2016).

Figure 1.5: Nanomaterial (For example: Carbon nanotube).
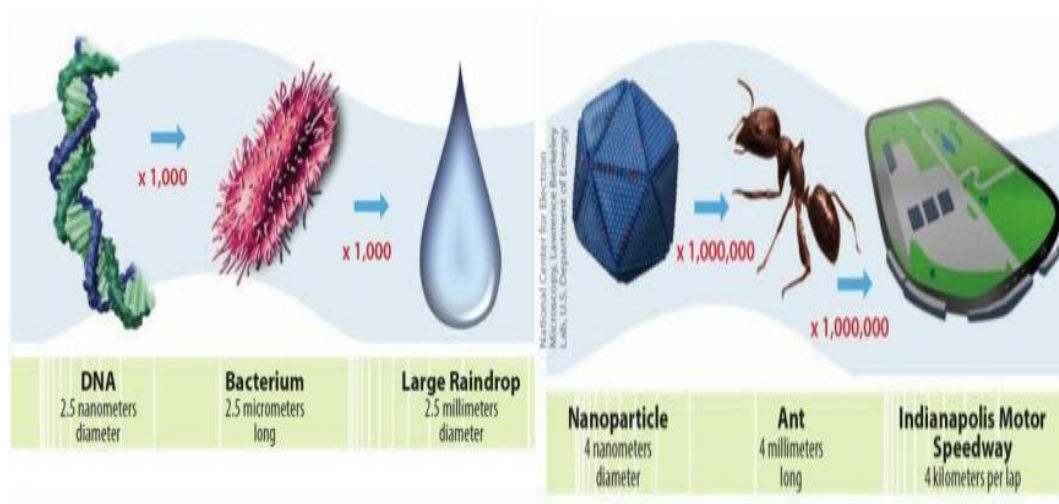
Figure 1.6: Comparing sizes at nanoscale

1.5.1 Occurrence of nanomaterials

Nano based materials of specific concern exists as manufactured nanomaterials while others occur naturally. Engineered nanomaterials (ENs) are usually created to, as well as to serve various marketable produces and methods. These ENs may exist in materials like sunglasses, makeups, sporting materials, pigment resistant clothing, tires, electrical devices and several daily materials utilized in the area of nanomedicine aimed at detecting, picturing and drug deliverance (Alagarasi, 2016).

Manufactured nano based materials are reserves devised at the nanoscale-molecular stage, their small size coupled with their unique features that are not commonly spotted on their large equivalence are used as an advantage. Nanomaterials have different properties due to two main reasons; new quantum effects and increased relative surface

area. Materials at the nano scale level have a considerably larger surface area to volume ratio than their conventional types, which can affect their strength and also proceed to better chemical reactivity. Also novel optical, electrical and magnetic behaviors can be harnessed due to determination of the material's properties and characteristics as a result of significant quantum effects at nano scale level (Alagarasi, 2016).

Nanomaterials are already utilized in the market, some having even been available for more than a few years or decades. The variety of viable products available in the present day is very wide, as well as wrinkle-free textiles and stain resistant, paints, varnishes, electronics, sunscreens and cosmetics. Nanocomposites and nano coatings are discovering applications in various end user produces, which include sports utilities, windows, automobiles together with bicycles. There also exist new UV-obstructive coverings on bottles made from glass that prevent brews from sunlight destruction. Nano TiO_2, discovering uses cosmetics, sun-preventive creams as well as nano based silica exists applicable in many materials for packing together with make-ups and medical (dental) packings (Alagarasi, 2016).

1.5.2 What is at nanoscale in nanomaterials?

Figure 1.7: Range of scaling of materials from tiniest scale to a complete human being
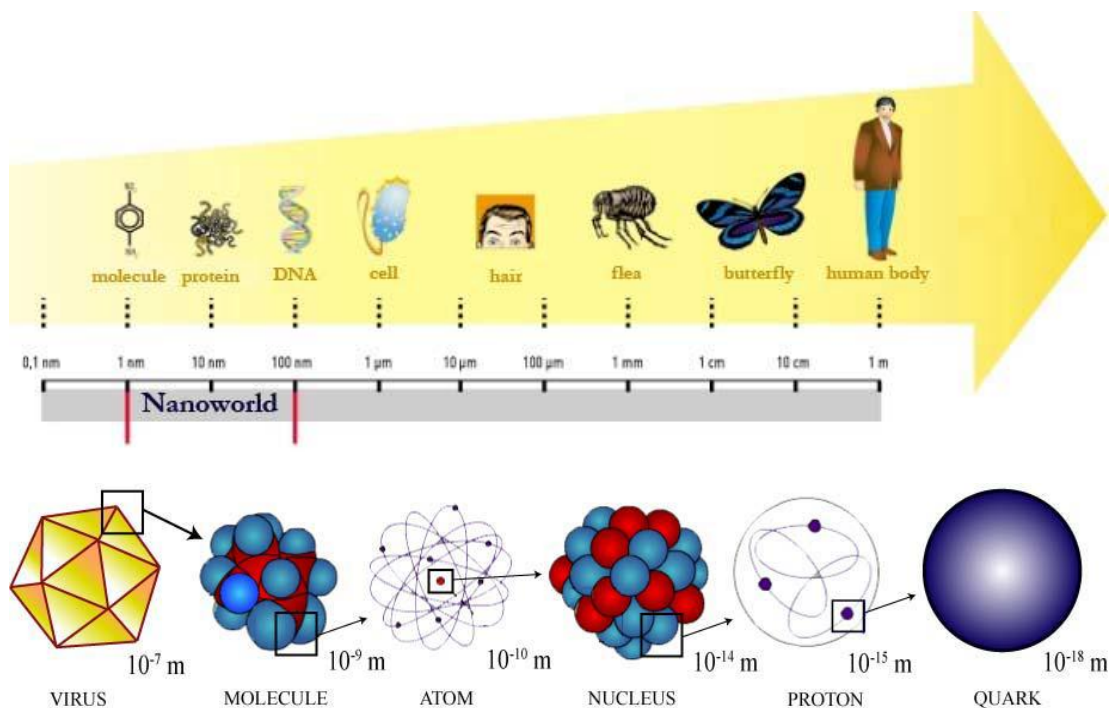
1.5.3 History of nanomaterials

Nanostructures were formed in the early meteorites big bang, and the discovery of nano based materials started instantly after the extensive report. Later on, the nature developed various other Nanostructures such as skeletons, seashells etc. In the early human's usage of fire nano scaled smoke particles were formed. However, later the scientific history of nanomaterials began. In 1857 Michael Faraday synthesized the colloidal gold particle which was registered as one of the first early scientific reports. Additionally, for over 70 years nanostructured catalysts studies have also existed. Hastened and stunk silica nano particulates were being produced then marketed in early 1940's as alternatives for ultrafine carbon black for rubber reinforcements (Alagarasi, 2016).

Applications of nano sized amorphous silica particles have made its way in various daily consumed products. Metallic nano powders used for magnetic recording tapes were established in 1960's and 1970's. For the first time, in 1976, Granqvist and Buhman produced and published nanocrystals method which is the now popular inert-gas evaporation technique. In recent times, discovery reveals Maya blue paint is made up of nanostructured crosslinked constituents. The origin of its biocorrosion properties, color, acids resistance is yet to be discovered. However, genuine trials examinations explain the constituent is composed sharp pointed crystals resembling a needle shape which make a super-lattice and additions of nano-metallic particulates. The blue color appears when the super-lattice and nanometallic particulates are existing, just as in the fabrication of synthetic samples (Alagarasi, 2016).

Nowadays nanoscale manufacturing increases in a fast-rising rate of fundamental and useful constituents organic and inorganic, paving way of controlling technical purposes. Manufacture of nanoscale materials is commonly centered on the design of detached minor clusters that are afterwards joined into a major-part material inserting into compressed matrix of solid or liquid component, for instance, nanoscale silicon, that is different from a normal silicon in property electronically and physical, may perhaps be useful to macroscopic semiconductor procedures in making novel appliances. A normal glass for example becomes a high performance optical medium with abled and possible uses in optical computing when it is doped with quantized semiconductor "colloids" (Alagarasi, 2016).

1.5.4 Category of nanoscale materials

Nano based materials exist in an extensively small dimension in which one dimension is 100 nm or below. They can be Nano-scaled in one dimension e.g. surface films, two dimensions e.g. strands or fibers, or three dimensions e.g. particles. They can exist in single, bonded (fused), aggregated or agglomerated (combined) forms with sphere-shaped, tubular, and asymmetrical shapes. Familiar examples of nano-scaled materials include fullerenes, CNTs, quantum dots and dendrimers. These materials possess uses in this technological field, thus, shows dissimilar features compared to chemically common substances (Alagarasi, 2016). Richard W. Siegel classified Nanostructured materials into 0-D, 1-D, 2-D and 3-D nano-scaled structures.
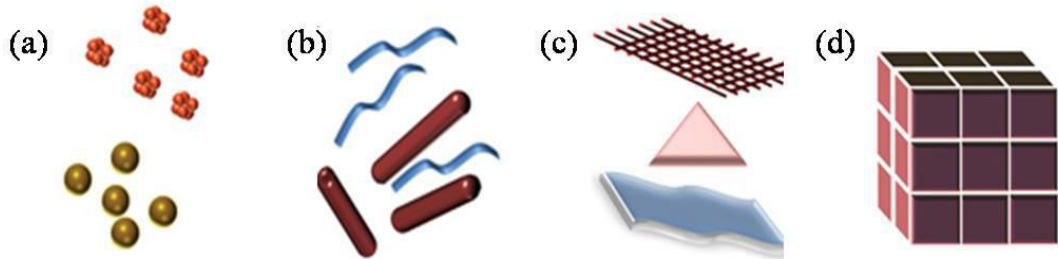
Figure 1.8: Category of Nanoscale materials (a) 0-D spheres and clusters; (b) 1-D nanofibers, nanowires, as well as nanorods; (c) 2-D nanofilms, nanoplates, also networks; (d) 3-D nanomaterials.

Ultra-fine grain size of less than 50 nm (< 50 nm) is used to characterize nanomaterials. This entails that nanomaterials are materials that are characterized by dimension limited to 50 nm. Richard Siegel defined nanomaterials as materials which can be manufactured in varieties of modulation of dimension: 0-D (atomic assemblies, filaments and bunch aggregation), 1-D (multilayers), 2-D (ultrafine-grained overlayers or buried layers), and 3-D (nanometer phase constituents containing equiaxed nanoscaled dimensioned grains) which was illustrated in figure 1.8 (Alagarasi, 2016).

1.5.5 Examples of nanoparticles and nanostructured constituents
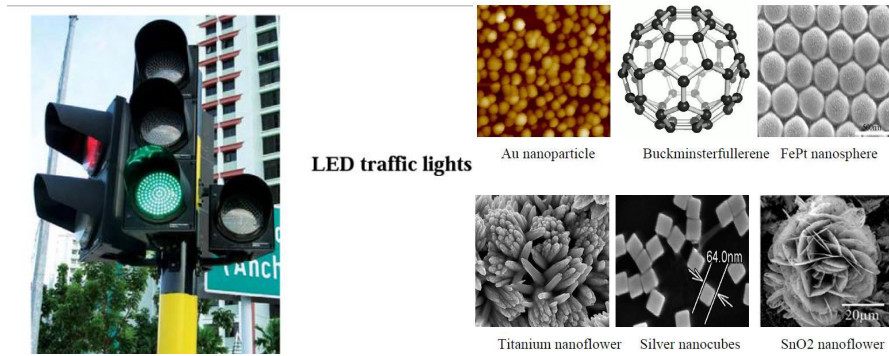
Figure 1.9: Examples of nanoparticles and nanostructured materials.
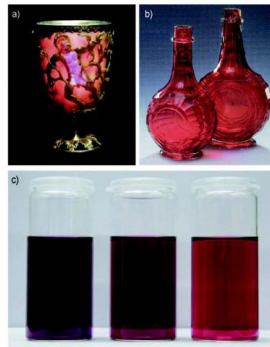
a) Late Roman Lycurgus cup, (b) baroque ruby glass (c) Colloidal Au nanoparticles.

1.5.6 Four major types of intentionally produced nanomaterials

There are countless kinds of deliberately manufactured nanomaterials, and varieties of others are anticipated to appear in the future. According to the U.S Environmental Protection Agency (U.S. Environmental Protection Agency, 2007), most recent nano based constituents can be arranged into four types:

i.   Carbon built constituents
ii. Metal built constituents
iii. Dendrimers
iv. Composites

Carbon Built Constituents

They are usually carbon containing nanomaterials, the majority usually in the form of ellipsoidal, hollow spheres, or tubes. Ellipsoidal as well as spherical nano-scaled carbon constituents are known as fullerenes and cylindrical nanomaterials referred to as

nanotubes. Thus, having various prospective functions, comprising applications in electronics, stronger and lighter materials, enhanced films and coatings.

Metal Built Constituents

Metallic nanoparticles comprise of nanogold, nanosilver, quantum dots including nano metallic oxides, like TiO_2. A material composed of several hundreds or several thousands of atoms closely packed semiconductor crystal and whose size is on the range of a few nanometers to a few hundred nanometers is known as quantum dot. The size of a quantum dot is crucial to its optical property as such altering the dimension of quantum dot alters its photosensitive property.

Dendrimers

Dendrimers are polymers of nanoscale range made from branched units. Specific chemical functions of a dendrimer can be attributed to the presence of various chain ends which could be beneficial for catalysis. Three dimensional dendrimers can also be useful in drug delivery due to their possession of inner openings to which other molecules can be positioned.

Composites

Nanoparticles combining with other nanoparticulate or with greater part-typed, larger constituents will give composite. Nano particulates, like nano dimensioned clays, are already being combined with produces extending from auto parts to packing tools, to improve mechanical, thermal, barrier, and flame-retardant properties.

1.5.6.1 Distinctive properties

Exceptional features of numerous kinds of deliberately manufactured nano scaled materials provide them unique catalytic, mechanical and many more characteristics which are extraordinarily needed in medical, marketable, environmental and soldierly divisions applications. They can additionally be useful in multifaceted nano-scaled assemblies and schemes. As novel functions for constituents with these distinctive features are recognized, the quantity of produces comprising these nanostructured materials and their potential functions is increasingly growing.

1.5.7 Synthesis of nanomaterials

Nanomaterials are generally classified based on two major production concepts; the "*Bottom-up*" and the "*Top-down*" approaches.

Bottom-up

Bottom – up is method of preparing nanostructure by assembling and consolidating distinct atoms and molecules into the structure. It is operated in a step-by-step chemical reaction which are governed by series of catalysts. The catalysts involved here are known as '*enzymes*', hence, it is a technique that is familiar in biology to construct living tissue which forms and supports the organs of the body by assembling amino acids.

Top-down

A *lithographical* method is used in this process. Here large scaled materials are gradually reduced (removal based method) to smaller sizes of nanoscale using lithography technique, that direct radiation through a template on to a surface covered with a radiation – sensitive resist after which resist is extracted out and the surface chemically treated to produce the nanostructure. Thus, this method is an opposite approach to bottom – up method and is hence referred to as top – down method.
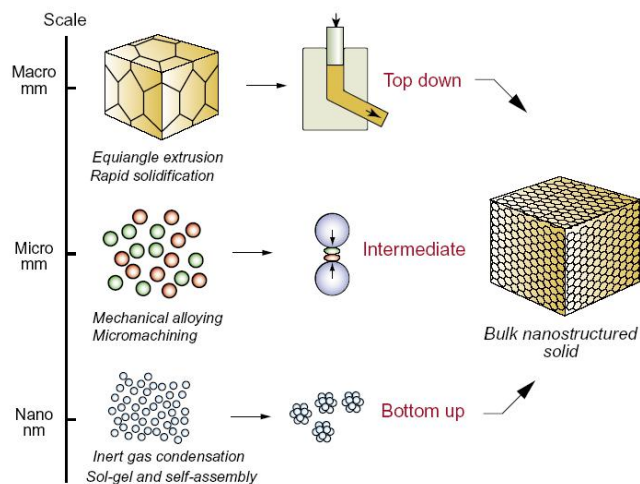
Figure 1.10: Bottom-up and Top-down synthesis of nanamaterials.

Figure 1.10 (continued): Bottom-up and Top-down synthesis of nanamaterials.

Moreover, as synthesis of nanoparticulate materials can be achieved by chemical approach (bottom-up) or the grinding approach (top-down), several techniques may be involved depending on nanoparticle's synthesis of interest. As described by Namita Rajput (Eview, 2015), these techniques include;

1. Gas condensation
2. Vacuum deposition and vaporization
3. Chemical Vapor Deposition (CVD) and Chemical Vapor Condensation (CVC)
4. Mechanical Attrition (ball milling)
5. Chemical Precipitation
6. Sol-Gel Techniques
7. Electrodeposition

1. <u>Gas Condensation</u>

Gas condensation technique has been the initial method utilized in nanocrystalline metals and alloys synthesis. In this method, thermal evaporation sources are utilized to vaporize a metallic or inorganic material at atmospheric rate of 1-50 mbar. These thermal evaporation sources may include a heated Joule recalcitrant containers and electron ray vaporization appliances.

A high residual gas pressure greater than 3 mPa (10 torr) in gas evaporation leads to the generation of ultra-fine particulate material (100 nm) and this is as a result of collision of evaporated atoms with residual gas molecules. Vaporization sources can be, elevated leveled energy electron rays, low energy electron beam, resistive heating and introductory heating. Bunch assemblies are generated at the area of the evaporation provider by homogeneous nucleation at the gaseous stage which rise with integration by atoms at the gaseous stage. It comprises of evaporation source of an ultra-high vacuum (UHV) fitted system, a compaction device and a bunch retrieval appliance containing liquid nitrogen scrapper aggregate. Atoms condense in super-saturation vicinity close to Joule heating during heating process. Nanoparticulate matter will then be extracted with scrapper as metal plate. Afterwards, evaporating with W, Ta and Mo recalcitrant metallic container (Tissue and Yuan, 2003). When the metallic constituents interact with the crucibles container, electron ray vaporization method should be utilized. This technique is exceptionally time-consuming. It also experiences limitation from situation like source and precursor inconsistency, limits in temperature as well as different vaporization limits in an alloy. Other alternate supplies were being discovered for years. An example, Fe is evaporated in inert gas environment of He. During interaction Fe atoms that was being evaporated condense as small crystals as a result of the loss in kinetic energy, thus these crystals aggregate to form unconfined powder. Laser evaporation and sputtering can be utilized in place of thermal evaporating technique (Hasany, Ahmad and Rehman, 2012). In sputtering method atoms are emitted from the surface as result of force received from attacking substances of atomic or molecular dimension. Distinctive sputtering utilizes a shining liberation or ion ray. In magnetron sputtering, the communication proceedings that happen at the interested region or surface and close to target surface during sputtering process have lead compared to diode and triode magnetron sputtering techniques. Greater amount of the plasma is

restricted to the near interested surface in magnetron sputtering. Sputtering electron beam heating and plasma techniques are other different energy supplies which was being effectively utilized to generate bunch of ultra-fine particulate materials. Different variety of clusters have been produced by the utilization of sputtering method in low pressure environments, such clusters include Ag, Fe and Si.

2. <u>Vacuum Deposition and Vaporization</u>

In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum. Materials are vaporized by the vaporization source by thermal processes at a pressure that is not greater than 1 mTorr at 10 – 0.1 MPa vacuum levels and to which temperature of the substrate goes ambient to 500°C. Equilibrium vapor pressure rather saturation of a substance is regarded as vapor pressure of the substance in stable state with solid or liquid surface. Sensible deposition proportion can be attained when the vaporization proportion is elevated. An important deposition rate is achieved with 1.3 Pa (0.01 Torr) vapor pressure.

Multi-body collisions in dense vapor cloud can lead to vapor phase nucleation occurrence. Atomic particles are dispatched over gas to make available essential colliding action and preservation for nucleation. Hence, particulate substances are known as ultra-fine particles or clusters and they are in the range of 1 to 100 nm (Gohil et al., 2007, Chang et al., 1994 and Winter, Hahn and Metallkd, 2003). Vacuum deposition offers economic benefits and high deposition rates. Although the deposition of many compounds was found to be difficult, however, nanoparticles manufactured from a super-saturated vapor are generally lengthier than the bulk cluster.

3. <u>Chemical Vapor Deposition (CVD) and Chemical Vapor Condensation (CVC)</u>

This has been a well understood method that involves deposition of a solid onto a heated surface through a reaction from vapor or gas stage. The CVC process needs activation energy so as to work to which various techniques may deliver. A high temperature of above 900°C is set to activate reaction in thermal CVD. Distinctive tools consist of deposition chamber, gas supply system and an exhaust system. In temperature ranges of 300 and 700°C, reaction is activated in plasma CVD, as well as pyrolysis occurring as the laser thermal energy tends to heat a substrate in laser CVD. An ultra violet radiation brings about chemical reaction in photo-laser CVD. This

radiation has adequate photon energy to split the bond in the reacting molecules, thus, the reaction is activated by photon in the process as well as deposition occurring at room temperature. CVD was used in the synthesis of composite powders and more so, SiH_4, CH_4, WF_6 and H_2 were used as supply for gas at $1400°C$ for the synthesis of SiC/Si_3N composite. However, CVC is another method that was developed in 1994 in Germany. It comprises pyrolysis of vapors of metal organic precursors in a less pressure environment. Particulate materials of ZrO_2, Y_2O_3 and Nano whiskers were being using CVC technique (Gohil et al., 2007, Chang et al., 1994 and Winter, Hahn, Metallkd, 2003 and Konrad et al., 2001). Using mass flow controller an organic precursor of metallic constituent is set into the hot region of the reactor. In the synthesis of SiCxNyOz powder for example, hexamethyl disilazane $(CH_3)_3$ Si NHSi $(CH_3)_3$ was utilized with the help of CVD method. Representative nanocrystalline materials that have being synthesized are shown in Table 1.1

Table 1.1: Nanobased crystalline representative materials synthesized using CVC

Precursor	Product Powder	Phase as prepared	Average particle size	Surface area
(CH3)3SiNHSi(CH3)3	SiCxNyOz	Amorphous	4	377
Si(CH3)4	SiC	β-phase	9	201
Al[2-OC4H9]3	Al_2O_3	Amorphous	3.5	449
Ti[I-OC3H7]4	TiO_2	Anatase	8	193
Si[OC2H5]4	SiO_2	Amorphous	6	432
Zr[3-OC4H9]4	ZrO_2	Monoclinic	7	134

Source: (Eview, 2015)

4. Mechanical Attrition

In contrast to the various techniques explained above, mechanical attrition synthesizes its nano based components using structural decomposition of rough grained components and not by cluster assembly due to plastic distortion. Basic Al powders and β-SiC have being synthesized in an elevated energy ball mill. In addition, not quite long, ceramic/ceramic nano based composite WC-14% MgO component was being invented. Ball and rod milling methods had established increasing recognition to be strong technique that can be used in the invention of numerous sophisticated products, and thus,

this technique belongs to the mechanical alloying process. Mechanical alloying process is an exceptional method that can be conducted at room temperature. This method could be conducted on different mill types, this include the high energy mills, the centrifugal mill type, the vibratory mill type and the low energy tumbling mill (Konrad et al., 2001, Rostislav and Andrievskii, 1994).

High energy mills comprise:

    i.   Attrition Ball Mill
   ii.   Planetary Ball Mill
  iii.   Vibrating Ball Mill
  iv.   Low Energy Tumbling Mill
   v.   High Energy Ball Mill

Attrition Ball Mill

In this method, an agitator that has a vertical rotator central shaft with horizontal arms (impellers) stirs the milling process at an effectively controlled milling temperature. The rotation speed is to later increase to 500 rpm.

Planetary Ball Mill

Centrifugal forces are triggered at the moment of supporting disc rotation and independent turning of the vial. The charge powder and the milling media rolls against the wall of internal vial and then bowled them off through the bowl at a rapid mode of 360 rpm.

Vibrating Ball Mill

Vibrating ball milling is generally aimed at producing amorphous alloys. At very high speed (1200 rpm) and a perpendicular direction, the transformations of fine particles and milling apparatuses are stressed.

Low Energy Tumbling Mill

They have low operation costs and simple to operate, and were being utilized for effective synthesis of alloyed fine particles of mechanical nature. A laboratory gauge rod mill is utilized in synthesizing uniform unstructured Al30Ta70 fine particles with

the help of S.S. cylinder rods. Single-stage unstructured fine particles of AlxTm100-x with less iron strength (concentration) can be produced with such procedure.

High Energy Ball Mill

Although high-energy ball milling was even before now a recognized tool, conversely, it was believed to be unclean due to iron impurity complications. Nonetheless, impurity levels to within acceptable limits have been achieved by the application of tungsten carbide constituent and inactive environment and /or high vacuum steps. Usual shortcomings include several extremely elevated spread size disseminations, low surface together with partly unshaped status of the fine particles. Such fine particles (powder) are extremely active with oxygen, hydrogen as well as nitrogen. This method advances to manufacture of alloys that are unable to be fabricated with conservative methods. It is impossible to fabricate an alloy of Al-Ta, due to factual reason that the variation in melting points of Al (933 K) and Ta (3293 K) through any conservative technique. Conversely, it can be produced by mechanical alloying with the help of ball milling technique.

5. Chemical Precipitation

Here, the dimension of the material is controlled by stocked precipitated process. Primarily, the strategy was to synthesize and study the nanomaterial in situ i.e. avoiding physical alterations and accumulation of minute crystallites in the same liquid medium. Double layer repulsion of crystallites controlled the thermal coagulation and Oswald ripening utilizing non-aqueous diluents at lesser temperatures for synthesis. And before precipitation reaction, dopant is added to the parent. Surfactant is utilized to sustain parting (separation) between the particulate materials generated. Nanocrystals are then parted by centrifugation, cleaned (washed) and dry in the vacuum. After drying, the dried synthesized material is further exposed to UV curing so as to polymerize the surfactant capping film onto the surface of the nano bunch in order to convey actual quantum imprisonment (Konrad et al., 2001, Rostislav and Andrievskii, 1994).

6. Sol-Gel Techniques

Sol-gel processing methods have also been comprehensively practiced in addition to the methods mentioned previously. Nanoparticles or ordinary molecules are much smaller

than colloidal particles. However, when mixed together colloidal particles appear bulky and to which nanoparticles appear always clear. It involves formation of colloidal suspension (sol) preceding to the evolution of networks and gelatin to form a network in unceasing liquid phase (gel). The colloidal consist of metallic alkoxides ions and alkoxysilanes as their precursor. Tetramethoxysilane (TMOS) and tetraethoxysilanes (TEOS) that give rise to silica gels are considered as the most widely used. Being water-immiscible, alkoxides are also organo-metallic predecessor of silica and aluminum, zirconium, titanium and much more. Firstly, in sol gel method a uniform solution of 1 or more interested alkoxides is involved, which are predecessors of silica and alumina, zirconia and titania and more. Accordingly, based on scientific findings, reactions are initialized by a catalyst as well as regulating P^H (Bhargava et al., 1994, Yu et al., 2001, Lu and Jangannathan, 2002 and Morita et al., 2004).

Namita Rajput (Eview, 2015) describes below the four stages that occur in sol gel technique:

   i.   Hydrolysis
  ii.   Condensation
 iii.   Growth of particles
 iv.   Agglomeration of particles

Hydrolysis

In hydrolysis, substitution of [OR] group with [OH] group usually happen as a result of addition of water. Oxygen on the silicon atoms in silica gel are attacked, which in turn causes hydrolysis. Addition of a catalyst can also hasten the hydrolytic process; such catalyst may include hydrochloric acid and ammonia solution. It lasts till all the alkoxy groups are substituted with hydroxyl groups. Successive condensational reactions comprising silanol group (Si-OH) will form siloxane links (Si-O-Si), alcohol as well as water. Finally, hydrolysis happens with the strike of oxygen on the silicon atom in the water.

Condensation

In this process for condensation to occur siloxane bond must polymerize which will definitely involve a reaction that produces water or a reaction that produces alcohol.

Monomers and dimers as well as cyclic tetramers and higher rings are formed after condensation. Hydrolysis proportion can be affected by reagent concentration, P^H as well as molar ratio of water/Silicon (H_2O/Si) i.e. when it involves silica gels. Additionally, the timing as well as the drying methods are significant. When these features are controlled, it would be promising to differentiate the component and properties of sol-gel formed complex.

Growth and Agglomeration

Siloxane aggregated molecules form a network during which the quantity of siloxane linkages rise in solution. When this happens, a gel is manifested after drying. Thus, network shrinks when water as well as alcohol are exhausted. Spherical nanoparticles are formed at P^H values greater than 7 and 7 – 5 range value of H_2O/Si and polymerizing to give siloxane linkages by producing water or alcohol.

$$2\ HOSi\ (OR)_3 \rightarrow (OR)_3\ SiOSi(OR)_3 + H_2O$$

Or

$$2\ HOSi\ (OR)_3 \rightarrow (OR)_2\ OHSiOSi\ (OR)_3 + H_2O$$
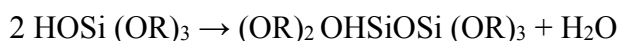
Silica particles sizes grow and more soluble at a P^H of above 7. However, at the stage where the solubility between smallest and largest particles cannot be differentiated, silica growth stops. At higher temperatures larger particulate materials are produced. Similarly, Zirconium as well as Yttrium gels can also be formed. In spite of developments in chemical as well as physical production processes, some drawbacks and restrictions still exist. Vaporizing technique of laser provides numerous benefits when compared to some heating methods. Laser of 106 – 107 W/cm^2 intensity and of high energy pulsed is powered on interested material. The plasma brings about high vaporization and elevated temperature of 10,000°C. A surface area of 0.01 cm^2 in 10-8s pulse, the typical atomic generations are 1014 – 1015 from the surface area. Hence a vapor of an elevated density is formed at a very much limited time (10-8 s) which should be utilized for uninterrupted deposition of particulate materials.

7. Electrodeposition

Electrodeposition is another technique for Nanostructured materials production. The films are uniform and strong as well as mechanically strong. Considerable improvement has been in existence in nanoscale structured coverings applied either by DVD or CVD. Several non-conservational methods like hypersonic plasma particle deposition (HPPD) were being in application in the production of nano particulate materials as well as its deposition. Importantly, possibility of nano particulate material production and applicability is practically not discovered. These materials provide various encounters to overpower. Designing better materials require understanding more of synthetic methods. A number of features of nano based structured deposits like hardness, wear resistance and electrical resistivity are strongly caused by particle dimension. The superior covering performance is caused by grouping of increased hardness and wear resistance (Dikusar et al., 2009 and Silkin et al., 2010).

1.5.8 Properties of nanoparticles

Nano based materials possesses the componential characteristics that exist amongst those of the containing atoms and the greater part of the material. Despite many micro-based structured materials possess related properties to the resultant greater part of the materials, characteristics features of nanomaterials are considerably poles apart from those of atoms and bulk materials. Such happens due to the nanometer dimension of the material that makes these materials: (i) huge portion of surface atoms; (ii) elevated energy of the surface; (iii) spatial imprisonment; (iv) lesser deficiencies that aren't available in the resultant greater part of the materials.

Nanomaterials have tremendously large surface area to volume ratio; this is as result of their small dimension. The large surface area makes them have more "surface" dependent properties more importantly when nanoscale materials are comparable to length, surface properties of the nanoscale materials will affect the whole material. Hence this will improve or modify the characteristic features of the bulk materials. For instance, metallic nanomaterials can be used as very active catalyst (photocatalyst for example). Sensor selectivity and sensitivity are improved by nanowires and chemical sensors from nanoparticles. Spatial confinement influence from the nanometer feature sizes of nanoparticles also brought about Quantum effects. Modification of the energy

band structure and charge carrier density in the materials can be made to a certain extent differently from their greater part which will aid in modifying the material's microelectronic and optical characteristic features. Example, LED as well as lasers of the quantum wires together with quantum dots have future potentials in optoelectronics. Another rapid emerging field is elevated density data saving with the help of quantum dot appliances. Lesser inadequacies are additionally significant factor in discovering characteristics of nano based materials. Nano based structures and nanos-caled materials offers good turn for individual purification processes in a way that the impure and intrinsic materials flaws shift close towards the surface during thermal annealing. As a result, the increased materials precision influences the properties of nanomaterials. For instance, certain nanomaterials chemical stability may be improved, and characteristics of nano based materials would be mechanically greater compared to the greater part of the materials. More so, outstanding mechanical features of CNTs were well documented. Nanomaterials have already been considered to have several novel properties as a result of their nanoscale size. Various innovative applications of nanomaterials that come from these new properties have been recommended. Alagarasi (2016), discusses the optical, electrical, mechanical and magnetic properties of nanomaterials, and below are some of the explanations.

Optical Properties

The most interesting and essential part of nanomaterials are their optical properties. Some of the applications of nanomaterials that involve their optical properties include photocatalysis, display, biomedicine, optical detection, laser applications, censoring, imagery, phosphor, solar cells and photo electrochemical applications.

Nanomaterial's properties dimension, shape, surface features and other changeable determine their optical properties. Other variables as mentioned may include nobbling and dealings with nearby environs or other nano based structures. Illustration of the changes in the optical characteristics of metal and semiconductor nano particulate material is given in Figure 1.11. With the CdSe nano particulate semiconductor, small alteration in dimension changes the absolute optical characteristics properties of the nano particulate matter. Optical properties of metal nano particulate matter change only a little when they are enlarged as seen for the various examples of gold particulate nano

spheres. Conversely, the optical properties of the nanoparticles change dramatically when anisotropy such as growth of nanorods is added to the nanoparticle.
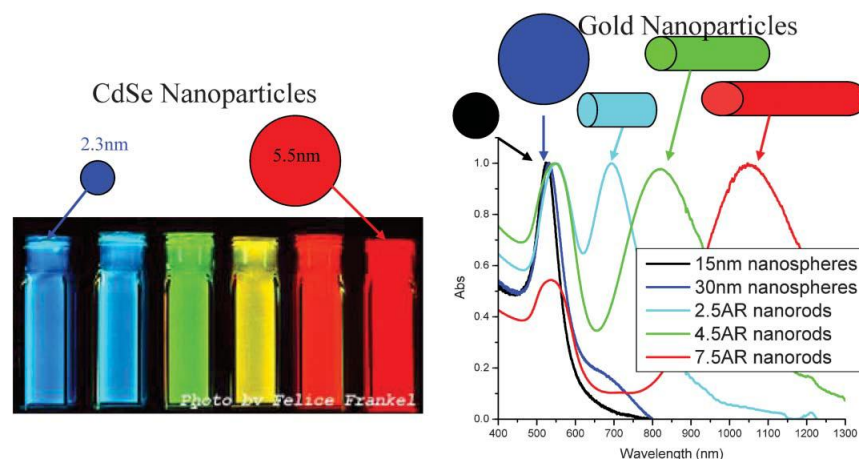

Figure 1.11: Fluorescence emission of (CdSe) ZnS quantum dots of different dimensions and absorption spectra of different dimensions and forms of particulate nano gold.

Electrical Properties

Nanoparticle's electrical property explains the fundamentals of electrical conductivity in nanotubes and nanorods, photoconductivity of nanorods, carbon nanotubes, and electrical conductivity of nano based composites. A fascinating technique that may be helpful in showing stages of conductance is the mechano-thinning of nanoscale wire and measurement of the electrical current at a fixed applied voltage. What is significant was that, by reducing width of the wire, number of electron wave manners supporting the electrical conductivity is turning out progressively lesser by well-described quantized steps.

Carbon nanotubes of electrical conductivity have one wave manner that transport electrical current. When the distance end to end and positioning of CNTs are not same, they tend to contact the surface of the mercury at various intervals, and thus, offers the following sets of info: (i) the influence of CNTs end to end distance on the resistivity; and (ii) the resistivity of the different CNTs. Seeing that the CNTs possesses various end to end distance, then alongside growing projection of the fiber package a growing range of CNTs will contact the mercury surface droplet as well as support to the electrical current conveyance.
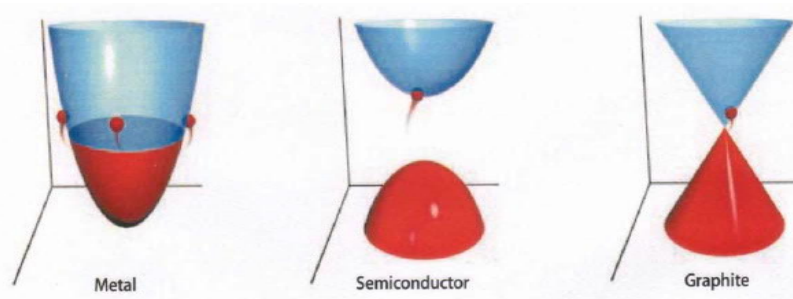
Figure 1.12: Electrical performance of naotubes.

Mechanical Properties

The aspect of nanoparticles properties that discusses whole metallic and ceramic materials including effect of porosity, effect of grain size, super plasticity, filled polymer composites, particle-filled polymers, and nanocomposites polymer filled with platelets, composites of carbon nanotubes is referred to as the mechanical property of nanoparticle. Producing macroscopic materials with high density and grain size in the range of less than 100 nm is difficult, this justifies why the discussion of mechanical properties of nanomaterials is to some extent of quite basic interest. On the other hand, two materials have attracted much greater interest as they will undoubtedly achieve industrial importance. Both of these materials are not produced by pressing and sintering.

These materials belong to the class of polymers that constitute nano particulates or nanotubes in order to help them enhance performance of their mechanical property, and rigorously plastic-deformed metals that present incredible characteristics. They are conversely generally not regarded as nanomaterials due to their large grain size. Investigational findings on the mechanical properties of bulk nanomaterials are largely weakened by major investigational drawbacks in generating specimens with precisely distinct grain sizes and porosities. Hence, perfect calculations and molecular dynamic findings are of main significance to the appreciation of the mechanical properties of these materials.

Mechanical properties of polymers are significantly enhanced when filled with nanoparticles or nanorods and nanotubes. Thus, those improvements largely depend on the kind of filler, and the way in which process was performed. The latter idea is of

exceptional concern, such that every specific benefit of a nanoscale particulate filler can be possibly gone if the filler accumulates, in that way imitating the large particles. Particulate filled polymer-based nanocomposites display a wide-ranging of failure strengths and strains. This solely depends on the shape of the filler, particles or platelets, and on the level of accumulation. In this class of material, polymers filled with silicate platelets show the paramount mechanical properties and are of the highest economic importance. Poor properties are obtained when the filler or agglomerates particles sizes increases. Experience shows that sometimes composites filled with nanofibers or nanotubes possess the least ductility and also potentially the best. However, there is a possibility of producing composite fibers with exceptionally high power and tension at rupture using carbon nanotubes. Amongst the highly motivating composites are the ceramic-based nanocomposites polymer, in which the ceramic stage is platelet-designed. Such kind of composite is desired naturally, as well as present in bones structure, in which it consists of crystallite mineral platelets of a small number of nanometers width joined together with collagen as the medium. Nanocomposites comprising matrix of polymer as well as defoliated phyllosilicates shows outstanding mechano-thermal characteristics.

Magnetic Properties

At nano size gold as well as platinum are considered magnetic, however, they are non-magnetic in bulk sizes. Although, bulk atoms exist differently compared to surface atoms, however, modification is viable with other chemical groups by covering the nano scaled particles. The latter fact unseals the likelihood of amendment, change or modifying the physical characteristics of the nano particulate matter by covering them with suitable molecules. In reality, it is expected the possibility that non-ferromagnetic bulk materials show ferromagnetism whenever prepared in nano scale. It may be possible for one to get magnetic nano based particles of Pd, Pt as well as the astonishing circumstance of Au (that is diamagnetic in bulk) from non-magnetic greater part of materials. Viewing the case of Pd as well as Pt, the ferromagnetism ascends from the conformational modifications linked to dimension effects.
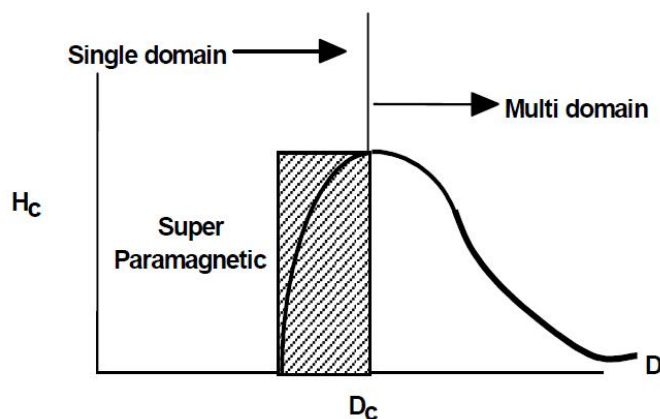
Figure 1.13: Magnetic properties of nano structured materials.

Nevertheless, gold nanoparticles turn out to be ferromagnetic when they are capped with proper molecules: the charge situated at the particle surface yields a ferromagnetic-like behavior.

Gold (Au) nanoparticles core and surface with diameter of 2 nm displays paramagnetic and ferromagnetic character respectively. These novel metals have large spin-orbit coupling which may harvest to a huge anisotropy, hence shows elevated instructing temperatures. Further astonishingly, for thiol-capped Au nanoparticles, enduring magnetism was detected up to room temperature. Nanoparticles of dimensions less than 2 nm have transporters situated in the *5d* band. Greater part of Au possesses a very limited density of conditions as well as becoming diamagnetic, thus the same stands for simple Au nanoparticles. Such statement recommends amendment of *d* band conformation by chemical bonding can persuade ferromagnetic such as metallic clusters characteristics.

1.6 Nano-Metallic Oxides and their Applications

The particle size dependent properties coupled with scientific and industrial applications of nano based structured crystal particulates have drawn tremendous concern for investigators in numerous fields of expertise. These materials present profoundly new chemical, magnetic, optical, electronic as well as mechanical properties that doesn't exist with their larger constituent parts (Hyeon, T., 2003). Various types of nano based structured crystalline particles were being utilized in catalysis (Kim et al., 2002), lasers (Eisler et al., 2002) photochemical reactions (Hagfeldt, A. and Gratzel, M., 1995), information storage media (Sun et al., 2000), and biological labeling and detection

(Scott *et al.*, 2002). Recently, tremendous research works have been given attention to the synthesis of homogeneous nano based structured crystalline particles of clearly described particle dimension to understand the dimension-supported characteristics (Hyeon et al., 2001, Hyeon et al., 2002, Murray et al., 1993 and Chen et al., 1997).

In the present era, zirconium (IV) oxide (ZrO_2) is currently considered as one of the familiar and important material in the ceramic industry. ZrO_2 and ZrO_2-containing materials have conventional applications in sands, powders, foundry ceramics and abrasion resistant materials. Moreover, oxygen sensors, catalysts, jewelry, fuel cells and resistive heating elements are some additional applications of ZrO_2 due to its oxygen-ion conduction and high refractive index (Mayo et al., 1999, Chraska et al., 2000 and Chen, 2009). The application of completely stable zirconia in fuel-cell technical knowhow used impressive ionic conductance of cubic zirconia at moderate and elevated temperatures (Chen et al., 2009). ZrO_2 possesses properties that include wear resistance, good hardness as well as thermal shock resistance as a result of toughness and increased strength. Such characteristics properties have resulted to the application of ZrO_2-based constituents in numerous manufacturing application areas, which include cutting tools, automobile engine components, as well as wire-drawing dies (Channu et al., 2011). Thus, ZrO_2 is recognized as a suitable material for thermal barrier coatings on metal components due to its relative elevated coefficient of thermal expansion and low thermal conductivity (Mayo et al., 1999).

TiO_2 in addition, is an oxide semiconductor catalyst that has proven to be the most suitable material for its powerful oxidation strength, non-toxicity, long term chemical stability and low cost (Ho et al., 2004). Other important metal oxides that present useful properties may include Tin Oxide (SnO_2) and bismuth oxide (Bi_2O_3) (Hicham et al., 2015 and Ashok et al., 2015). Tin oxide receives its recognition due to some of its properties like wide band gap (Eg = 3.64 eV, 330 K), high transparency in the visible range (>80 %) and *n*-type conductivity. SnO_2 crystallizes in rutile structure and can be produced in many different shapes and sizes using different low-cost synthesis techniques relevant for a verse range of applications such as, flat panel displays, solar energy cells, solid-state gas sensors (Ying et al., 2004 and Technology, 2013). Increased recognition and consideration is seen in Bismuth-based semiconductors as photocatalysts which breakdown organic pollutants in the presence of UV–vis light

(Cao et al., 2012, Pan et al., 2008, Xiaohong, Wei and Weidong, 2007, Weidong et al., 2007, Sirota et al., 2012, Shenawi-Khalila et al., 2012, Nguyen-Phan et al., 2011 and Lachheb et al., 2002). In essence and particularly, bismuth oxide (Bi_2O_3) (Zhou et al., 2009, Cheng et al., 2010 and Zhang et al., 2006) has various admiring properties, including high refractive index, high band gap (2–3.96 eV) and photoluminescence, and this oxide has applications in a range of areas including gas sensors, high temperature superconductor materials, solid oxide fuel cells, catalysis and functional ceramics (Pan et al., 2008 and Xiaohong, Wei and Weidong, 2007).

In an earlier article (Ralphs et al. 2013); it was proposed that mechanochemical synthesis is a method that promises for the synthesis of catalysts with emphasis in energy, conservational and chemical analysis applications. In contrast to today's common multistep diluent based preparation paths, several advantageous methods were preferred. As a technique for the preparation of photocatalysts of heterogeneous nature, mechanochemistry deserves greater recognition as a result of its easiness and to the reason that it produces importantly more reactive/excellent catalysts (Cao et al., 2012). The input of mechanical energy initiates mechanochemical reactions in this method, and this is achieved using simple crushing of 2 solids placed in a crucible and pestle, or by its enhanced technical form, the high-energy ball milling (Ivetic et al., 2015).

Binary semiconducting oxides, such as tin oxide (SnO_2) and zinc oxide (ZnO), have the ability to be utilized in various functions like photocatalysis, solar cells, and gas censoring as a result of their peculiar characteristic (Review, 2011, Wu et al., 2011 and Hou et al., 2014). Removing organic pollutants from wastewaters can be achieved by a promising alternative method which is the illumination of semiconductors as photocatalysts. Recent research (Firooz, Mahjoub & Khodadadi, 2011 and Wang et al., 2004) showed that combined oxide semiconductors, such as SnO_2/ZnO, can be more effective compared to the single photocatalysts (Dodd et al., 2006). Moreover, ternary types of such oxides can also be considered too as a result of a common perception that they favor more chances in designing materials for intended utilization (Wu et al., 2011), as their physical and chemical properties are more easily tailored compared to the binary oxides. Bismuth oxychloride (BiOCl) is an important nanocomposite material, which has manifold applications in make-up pigments, batteries, pharmaceutical industry, photocatalysis, optoelectronic and photovoltaic materials acting as lighting

diodes, lasers, solar cells, degradation of organic pollutants, CO_2 photo reduction, and many more (Ascencio-Aguirre *et al.*, 2017).

In this work single pure SnO_2, TiO_2, ZnO, Bi_2O_3 and ZrO_2 were synthesized using sol-gel and co-precipitation methods, and while solid state technique was used to prepare binary oxides of ZrO_2-Bi_2O_3, TiO_2-Bi_2O_3, ZnO-Bi_2O_3 respectively. Also, bismuth oxychloride (BiOCl) nanocomposite was also prepared. All samples were identified and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and the scanning electron microscopic analyses (SEM).

2. MATERIALS AND METHODS

In this chapter the methodology of the overall synthesis and characterization was explained. Furthermore, the chemicals/materials and the equipments used were also presented.

<u>Chemicals</u>

1. Tin (II) chloride dihydrate ($SnCl_2.2H_2O$, M=225.63g/mol), Merk 98-101%
2. Ammonium hydroxide solution, 25% (NH_4OH, 25%), Merk KGaA
3. Synthesized powdered forms of zirconium (IV) oxide (ZrO_2), bismuth (III) oxide (Bi_2O_3) and zinc oxide (ZnO)
4. Aldrich titanium (IV) oxide (TiO_2 nanopowder 21 nm primary particle size, ≥99.5% trace metals basis)
5. Bismuth (III) triacetate Crystalline, $Bi(CH_3COO)_3$, Alfa Aesar GmbH & Co KG
6. Sodium hydroxide (NaOH), Merk ≥99%
7. Bismuth (III) nitrate pentahydrate, ACS, 98% Crystalline, $Bi(NO_3)_3 .5H_2O$, Alfa Aesar GmbH & Co KG.
8. Zirconium oxynitrate hydrate, $Zr(NO_3)_2.xH_2O$, Fluka – Assay ~ 27% (Zr, gravimetric)
9. Titanium (IV) isopropoxide, ($C_{12}H_{28}O_4Ti$), Fluka [MP 14-17°C (Lit.); BP 104°C (Lit.)]
10. Zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$, Merk
11. Acetone, Merk KGaA
12. Ethanol, Merk KGaA

<u>Equipments</u>

1. Retsch MM200 ball milling equipment
2. Termal Laboratuvari Aletleri digital drying oven
3. Normal drying oven
4. Protherm furnaces Calcination machine
5. Sonamak ultrasonic cleaner
6. VELP Scientifica – AREX heating magnetic stirrer
7. Electrically digital weighing balance

8. Pestle and mortar
9. Different sizes of beakers, burettes, conical flasks, measuring cylinders, funnel and of course distilled water.

2.1 Experimental

2.1.1 Synthesis

Sol-gel synthesis of Tin (IV) Oxide (SnO₂)

Tin (IV) oxide synthesis was started by dissolving 3.0 grams of Merk 98-101% tin (II) chloride dihydrate ($SnCl_2.2H_2O$, M=225.63 g/mol) in a round bottom flask containing 50 mL distilled water and stirred for 20 minutes. Secondly, 4 mL of 25% ammonium hydroxide solution (NH_4OH, 25%) was added at a coordinated rate of 0.1 mLmin^{-1} with continues stirring and at P^H of 1 to 10.2 maintained at 70°C. After 2 hours stirring, the sol was set at room temperature for 48 hours which becomes neutral (after 2 days) and then washed with ethanol. The gel was pre-calcinated with microwave radiation for 5 minutes at 100 watts and with gap period of 1 minute after which was dried at 110°C for 20 hours. The sample was grinded with mortar and pestle after drying, and calcination was done for 2 hours at 400°C.

Sol gel synthesis of titanium (IV) oxide (TiO₂)

The sol gel synthesis of pure TiO_2 was initially started by drop-wise slow addition of 1.5 mL $TiCl_4$ into 15 mL ethanol at room temperature. Considerable quantity of HCl gas was expended during mixing. A light-yellow solution was achieved, which was left for days to form sol-gel. And the gel was finally oven dried at 105°C for 24 hours, grinded into fine powder and calcined at 600°C for 4 hours.

Co-precipitation synthesis of Zirconium (IV) oxide (ZrO₂)

A suitable quantity of zirconium (IV) oxynitrate hydrate was dissolved in deionized hot water and the mixture was subsequently heated until 65°C. A precipitate was formed by gradually adding NH_3 solution (25 wt %) up to a P^H value of 10. Subsequently, the solution was stirred slowly for 2 hours at 65°C. Then, solution was treated with 500 W microwave for 3 minutes. A precipitate was formed, after which was then filtered and

washed with deionized water and dried at 100ºC for 20 hours and calcined at 500ºC for 5 hours.

Synthesis of Bismuth (III) oxide (Bi$_2$O$_3$)

0.97 grams of bismuth (III) nitrate was dissolved in 10 mL of distilled water and stirred for 10 – 15 minutes. A prepared solution of 100 mL 0.2mol/L NaOH was added and maintaining a P^H of 11. The mixture was heated at 75ºC for 2 hours, filtered and washed with ethanol and distilled water for 2 – 3 times. Then, dried at 80ºC for 2 hours and finally calcined at 480ºC for 2 hours.

Synthesis of Zinc oxide (ZnO)

A 2.677 grams of Zn (NO$_3$)$_2$.6H$_2$O was dissolved in 15 mL distilled water, which was stirred in ultrasonic bath for 10 minutes at 50ºC. The solution was heated using magnetic stirrer at 65ºC for 2 hours, and ammonia solution was used to adjust the P^H to 10. Then, filtered and washed for 2 – 3 hours, which was dried at 100ºC for 20 hours and calcined at 500ºC for 3 hours.

Solid state synthesis of ZrO$_2$-Bi$_2$O$_3$/TiO$_2$-Bi$_2$O$_3$/ZnO-Bi$_2$O$_3$

Cumulative 0.3 grams of synthesized forms of zirconium (IV) oxide (ZrO$_2$), bismuth (III) oxide (Bi$_2$O$_3$), zinc oxide (ZnO) and Aldrich titanium (IV) oxide (TiO$_2$ nano powder 21nm primary particle size, ≥99.5% trace metals basis) were used. ZrO$_2$ and Bi$_2$O$_3$, TiO$_2$ and Bi$_2$O$_3$, ZnO and Bi$_2$O$_3$ were mixed respectively in the ratio of 1:1. The sample particles was grinded until homogeneity was attained after which it was diluted with ethanol, stirred and left to dry for some minutes. Drying was done for 1hr 30 minutes at 110ºC and grinded. Calcination was done for 6 hours at 450ºC.

Preparation of Bismuth oxychloride (BiOCl) nanocomposite

9 mmol solution of Bismuth triacetate [Bi (CH$_3$COO)$_3$] in 17.5 mL ethanol was prepared. 4.5 mmol solution of tin chloride dihydrates (SnCl$_2$.2H$_2$O) and 6 mL acetone was added to the 9 mmol solution and the mixture was stirred for 5 hours and aged for 24 hours (1 day) at 90ºC and calcinated at 500ºC for 2 hours.

2.1.2 Materials and characterization

X-Ray Diffraction (XRD)

X-ray crystallography or crystallography is a scientific discipline by which X-ray diffraction technique utilizes to investigate or discover crystal structures. The discovery of the phenomena that X-ray was diffracted by crystals was its origin. Having a history of more than hundred years, X-ray crystallography originated in a discovery of the phenomena that X-rays are diffracted by crystals. Several analytical methods centered on X-ray diffraction have been establish together with the advances of X-ray sources, beam-collimating optics, detectors, mathematical algorithms and computers. These methods are used to find out site of atoms in a crystal with a correct order of 10^{-4} nm (1 nm=10^{-6}). Crystal phases of several different materials and quantitative phase analysis can be determined using these techniques. X-ray diffraction methods lead in revealing the three-dimensional atomic structure of crystalline solids. The characteristics properties, function and purpose of materials heavily depend on their crystal structures. Thus, X-ray diffraction techniques have been broadly used as essential means in materials research, growth and manufacture.

Principles of X-Ray diffraction:

- X-rays are channeled over a crystallite material, thus, the patterns created shows info of result or data of dimension and form of the unit cell.

- X-rays channeling over a crystallite will bend at several different angles: this method is known as diffraction.

- X-rays work together with electrons in matter; this means that they are dispersed by the electron clouds of atoms.

- Angles to which X-rays are diffracted are dependent upon the distance between adjacent layers of atoms or ions. When X-rays come in contact with adjacent layers, their constructive energies can be added when they are "in phase". The latter creates dark dots on an indicator plate.
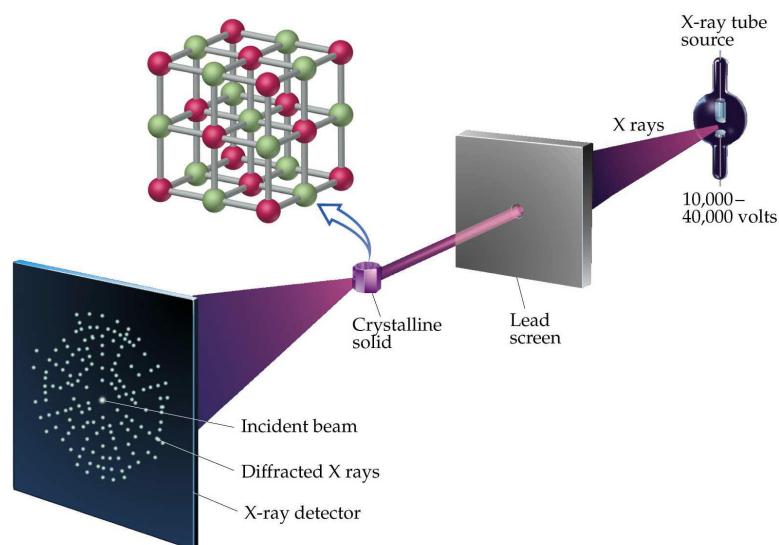
Figure 2.1: X-Ray diffraction of crystalline solid.

The equation of Bragg's law (1) as formulated by William Lawrence Bragg, connects wavelength with angle of incidence and lattice spacing, where *'n'* is a numeric constant known as the order of the diffracted beam, *'λ'* is the wavelength of the beam, *'d'* denotes the distance between lattice planes, and *'θ'* represents the angle of the diffracted wave. The conditions given by this equation must be fulfilled if diffraction is to occur (Lin and Barron, no date).

$$n\lambda = 2d \sin(\theta)$$

(1)

X-ray diffraction of crystal phases are obtained by a Rigaku D/Max-2200 diffractometer using CuKα (λ = 1.5406) radiation. Samples were scanned in the range of 10 to 60 at a rate of 0.5°/min (in 2θ). The Scherer equation (D = Cλ /βcosθ) is used to determine the sizes of the crystalline domains. The *'λ'* is the X-ray wavelength (Å), *'β'* is the full width at half maximum, *'θ'* is Bragg angle, *'C'* is a factor based on crystallite shape (taken to be one), and *'D'* is the crystallite size (Å).

Scanning Electron Microscope (SEM)

The highest significant magnification attainable using a conservational optical microscope is about 1000x. The wavelength of the imaging radiation must be reduced

so as to have the best resolution (as well as greater significant magnification). Electron are normally accelerated to high energies in electron microscopy, such energies are in the middle of 2 and 1000 keV (i.e. wavelengths of 0.027-0.0009 nm).

There exist various potential communications between the elevated-energy electron rays as well as the atoms in the sample. Electrons may pass through the specimen unabsorbed if the specimen is very thin, which in turn uses it to create imagery in TEM. When thicker specimens are being used, electron will not pass through and but only particles i.e electrons, x-rays and photons evolving from the surface can deliver info. Those are the indications utilized in a conservational SEM.

What are the reasons we need scanning electron microscopy?

Scanning electron microscope is able offer data on the surface of a crystallographic material, topography, chemical arrangement and electrical performance of top 1 μm of a sample. A number of particular stages (e.g. hot, cold or designed to permit in *situ* mechanical testing) can be involved to allow performance in several situations to be studied. Example, emission of light known as cathodoluminescence at close to absolute zero temperatures is far strengthener compared to room temperature, thus imageries made from the light produced or radiated by a cold sample are considerably less noisy.

Other leads of SEM over optical microscopy are:
- SEM gains from a huge depth of field, as such whatever the surface roughness most of the specimen surface is at the same time in focus. Optical microscopes operating at high magnification have a very small depth of field, and hence image quality is very dependent on the surface being smooth.
- Higher magnification of 1,000,000x can be achieved as well as a definitive resolution of 1 nm. Optical microscope's maximum significant magnification is around 1000x.
- There is chance of having more data than just the surface topography, e.g. crystal structure, chemical composition and electrical properties. Information can be cross-correlated with confidence offered by different imaging methods.

Leads of SEM over TEM are:

- Huge samples (200 mm diameter wafers, or even greater in distinctively adapted SEMs), than to 2.3 mm or 3 mm of diameter for TEM.

- SEM is not damaging to the assessment of the sample (TEM is efficiently a damaging method due to the sample formulation needed).

- SEM sample formulation time is very short (could be just a few seconds) whereas the sample is supported to a "stub" (sample holder). Sample formulation in TEM is more difficult as well as takes too much of time.

Morphology and size distribution of the photocatalysts were documented by scanning electron microscopy (JEOL/JSM-6335F).

Fourier Transform Infrared Spectroscopy (FTIR)

Wilbur Kaye began the use of infrared spectroscopy during the 1950's. He had invented a machine that verified the near-infrared spectrum and offered the principle to explain the findings. In 1960's, IR Spectroscopy became a recognized method there by paving way for Karl Norris to start using IR Spectroscopy in the analytical world. Several developments in IR Spec. include and most notably the applications of Fourier Transformations to this method, thus establishing an IR technique that had higher resolution and less noise. It was recognized as a method in an IR technique in the late 1960's.

An analysis that deals with infrared light interacting with a molecule is referred to as Infrared Spectroscopy. It can be measured in three ways; either by analyzing absorption, emission and or reflection. Organic and inorganic aspects of chemistry are the major areas where this method is applicable. Variations in atoms can be conferred using IR Spectroscopic technique, and on the basis of that functional groups in molecules can be determined. Usually, light atoms and stronger bonds will vibrate at a high stretching frequency (wavenumber).

In infrared spectroscopy light is utilized (infrared zone of the electromagnetic spectrum) that possesses a lengthier wavelength as well as a shorter frequency than visible light. Infrared spectroscopy comprises a collection of methods, typically centered on absorption spectroscopy. It significance spans through identifying and analyzing chemicals as with all spectroscopic methods. The technique or method of infrared

spectroscopy uses an infrared spectrometer to produce an infrared spectrum for a given sample that may be solid, liquid or gas. A simple IR spectrum is fundamentally a graph of infrared light absorbance (or transmittance) on the vertical axis and frequency or wavelength on the horizontal axis.   Units of frequency used in IR are typically reciprocal centimeters (sometimes called wave numbers) with the symbol cm^{-1}. Units of IR wavelength are generally given in micrometers (formerly called "microns"), symbol μm, which are related to wave numbers in a reciprocal way.   A common laboratory instrument that uses this method is a Fourier Transform Infrared (FTIR) spectrometer.   The photocatalyst absorbance was measured by Cary 500 UV–vis spectrophotometer.

Brunauer, Emmett and Teller (BET)

Powders and porous materials surface areas are established usually using the method of Brunauer, Emmett and Teller (BET). Generally, nitrogen gas is engaged as the probe molecule and is to be exposed to a solid under study at liquid nitrogen situations of 77K. Solid surface area is evaluated from the measured monolayer capacity and knowledge of cross-sectional area of the molecule that was used as a probe.

3. RESULTS

3.1 Characterization of SnO₂, TiO₂, Bi₂O₃, ZrO₂ and ZnO

Figure 3.1 shows XRD pattern of the sample of SnO_2. The mean crystallite size (D) of each nanoparticle for all the prominent planes (110, 101, 200, 211, 220, 002, 310, 112 and 301) was estimated using the Debye-Scherer formula as follows:

$$D = \frac{C\lambda}{\beta Cos\theta}$$
(2)

where C, λ, β, θ are the constant usually with a value of 0.9 or 1, the X-ray wavelength of radiation used (Cu/K$_\alpha$= 1.54056Å), the full width at half maximum (FWHM) of diffraction peak and the Bragg diffraction angle, respectively. The spacing between diffracting planes (d values) of SnO_2 sample was calculated from Braggs equation ($2d.\sin\theta = n\lambda$).
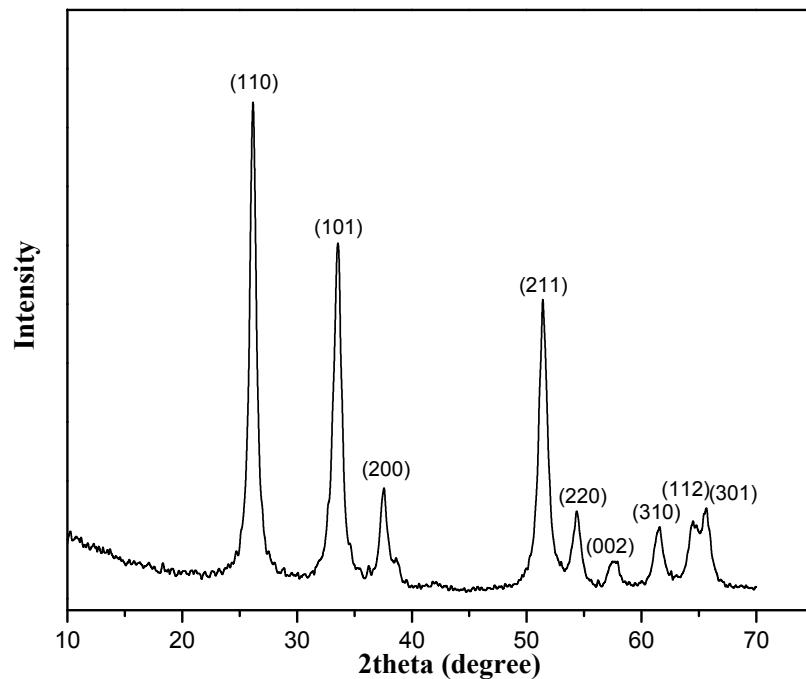

Figure 3.1: XRD pattern of tin (IV) oxide nanoparticles synthesized by sol-gel method.

Table 3.1: Comparison on *d*-values of JCPDS and calculated *d*-values of SnO_2 obtained

Standard values (JCPDS 21-1250)	Obtained *d*-values	Planes
3.350	3.3997	110
2.644	2.6661	101
2.369	2.3915	200
1.765	1.7761	211
1.678	1.6875	220
1.593	1.5922	002
1.498	1.5047	310
1.439	1.4436	112
1.415	1.4203	301

Moreover, the XRD results of all single pure oxides of TiO_2, Bi_2O_3, ZrO_2 and ZnO were presented in Figure 3.2. The crystallite sizes, morphology and BET surface area were given in table 3.2. Additionally, SEM images followed respectively in Figures 3.3, 3.4 and 3.5.

Table 3.2: Morphology, crystallite sizes and surface area of single pure catalysts

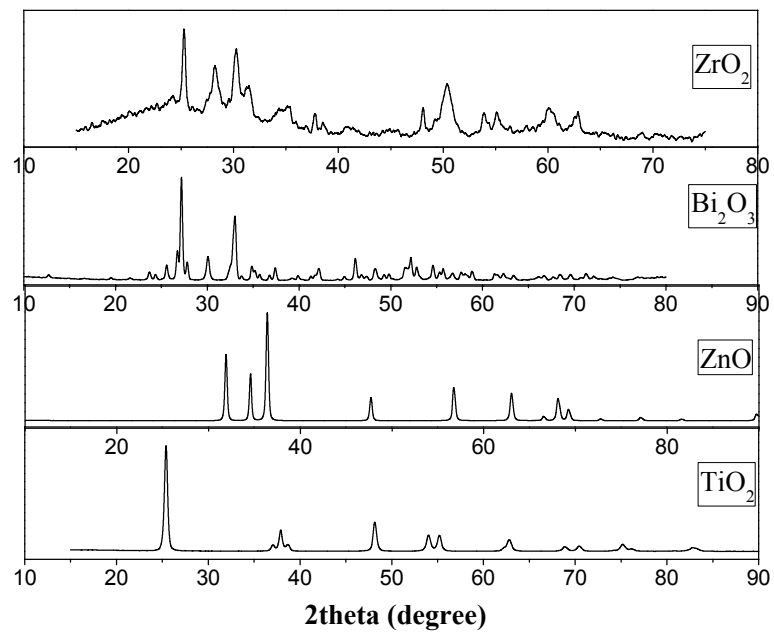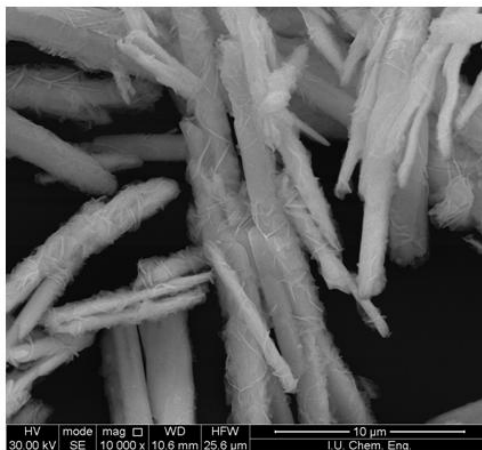| Catalysts	Crystallite size (nm)	S_{BET} (m^2g^{-1})	Morphology
SnO_2	12	155	Tetragonal
α-Bi_2O_3	42	2	Monoclinic
TiO_2	43	40	Anatase
ZnO	65	28	Hexagonal
ZrO_2	7	96	Tetragonal

Figure 3.2: XRD pattern of synthesized pure ZrO_2, Bi_2O_3, ZnO and TiO_2
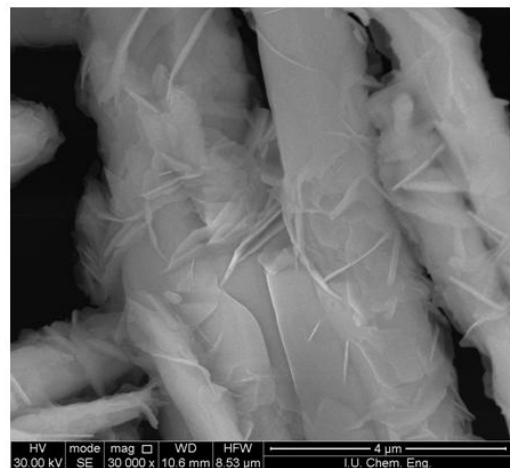

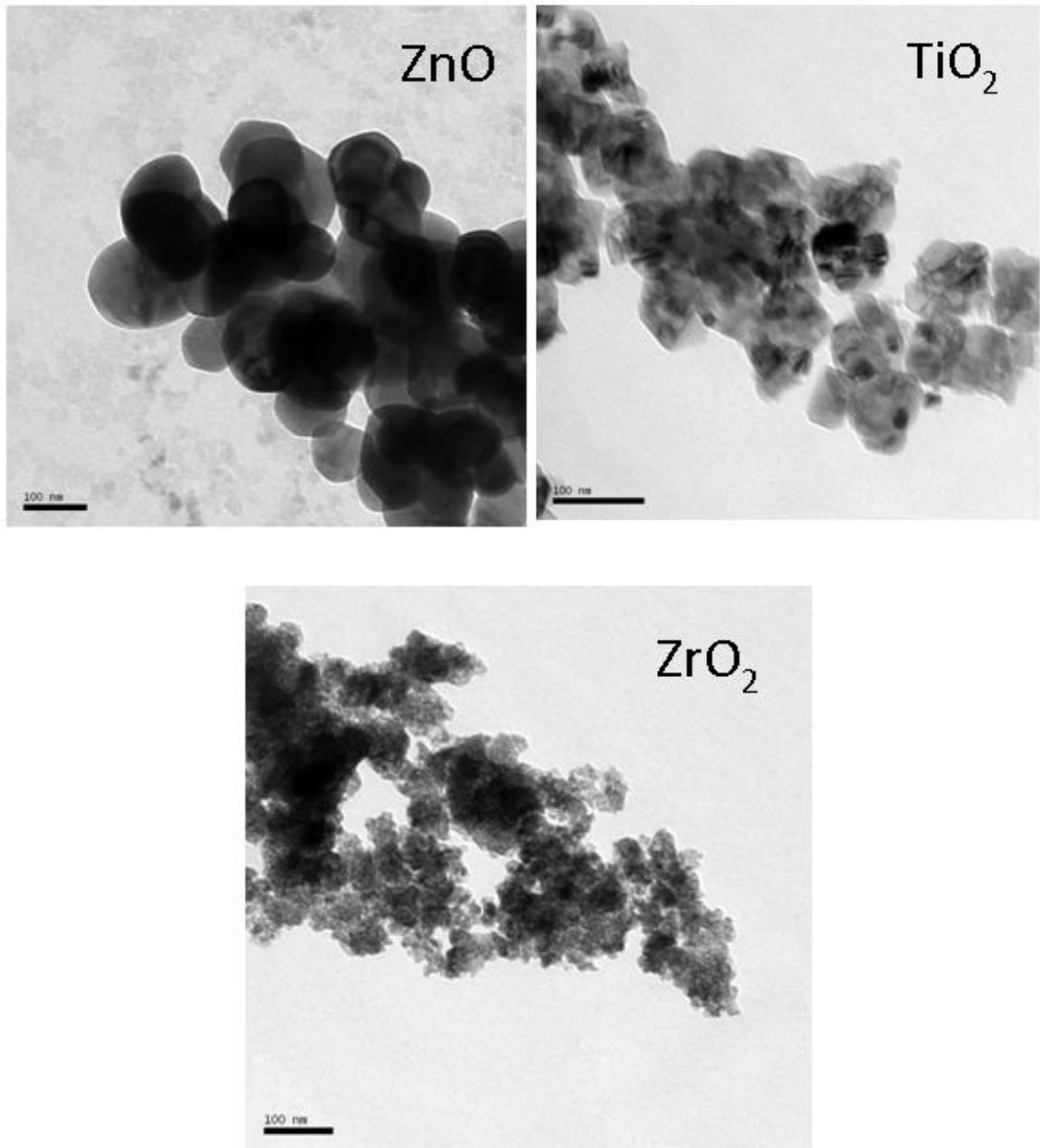**Figure 3.3:** SEM images of synthesized Bismuth (III) oxide.

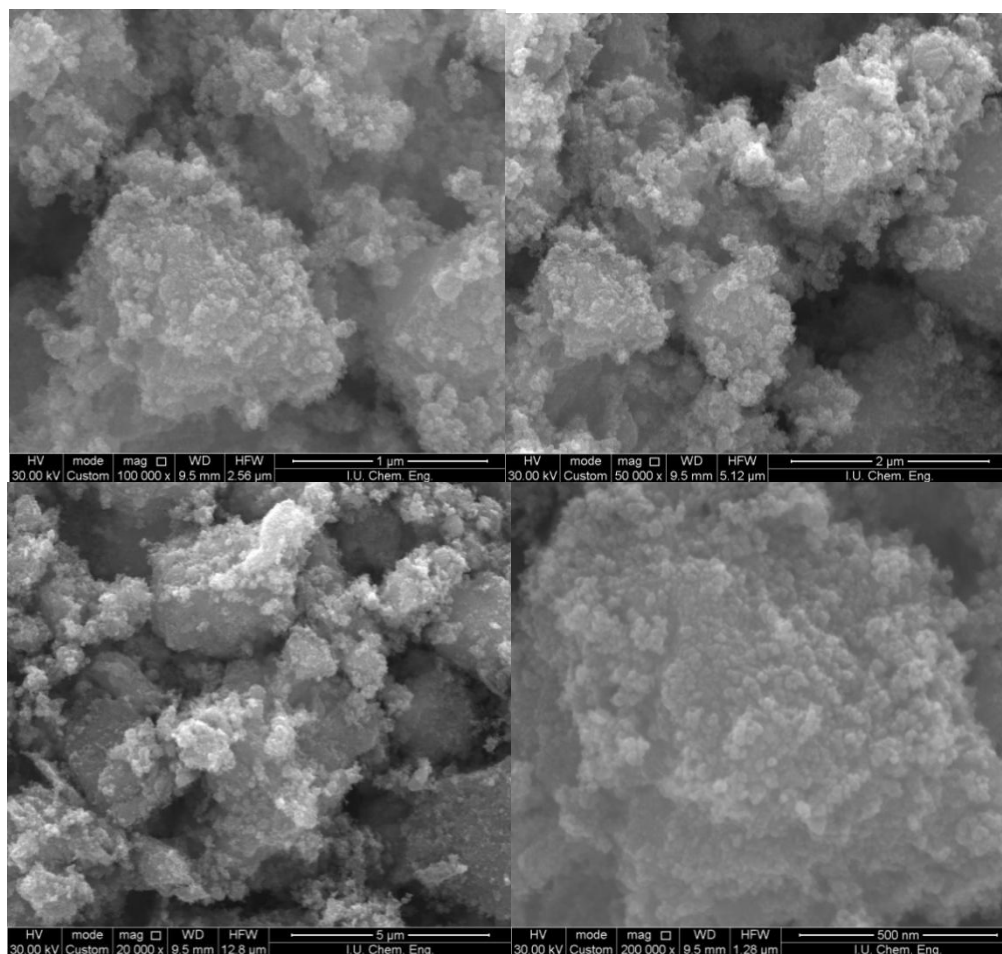**Figure 3.4:** SEM images of synthesized ZnO, TiO_2 and ZrO_2.

Figure 3.5: SEM images of synthesized tin (IV) oxide with different magnifications.

3.2 Characterization of TiO$_2$-Bi$_2$O$_3$ Binary Oxide

The XRD results of TiO$_2$-Bi$_2$O$_3$ binary oxide were explained in Figure 3.6. The morphology of as-synthesized TiO$_2$-Bi$_2$O$_3$ binary oxide (Figures 3.7) catalysts were examined with SEM analysis. However, FT-IR spectrum of prepared TiO$_2$-Bi$_2$O$_3$ binary oxide was demonstrated in Figure 3.8.
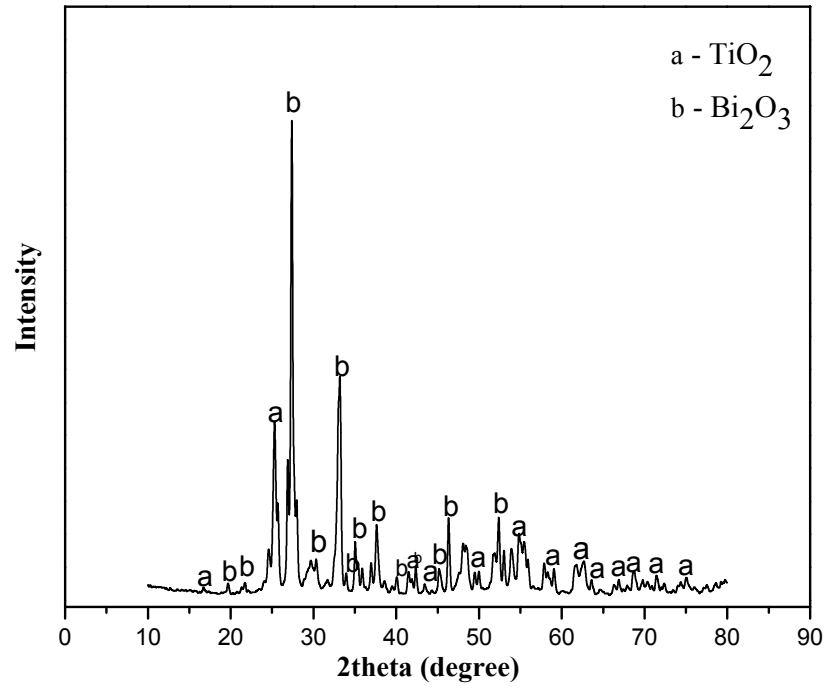
Figure 3.6: XRD pattern of synthesized TiO_2-Bi_2O_3 binary oxide.

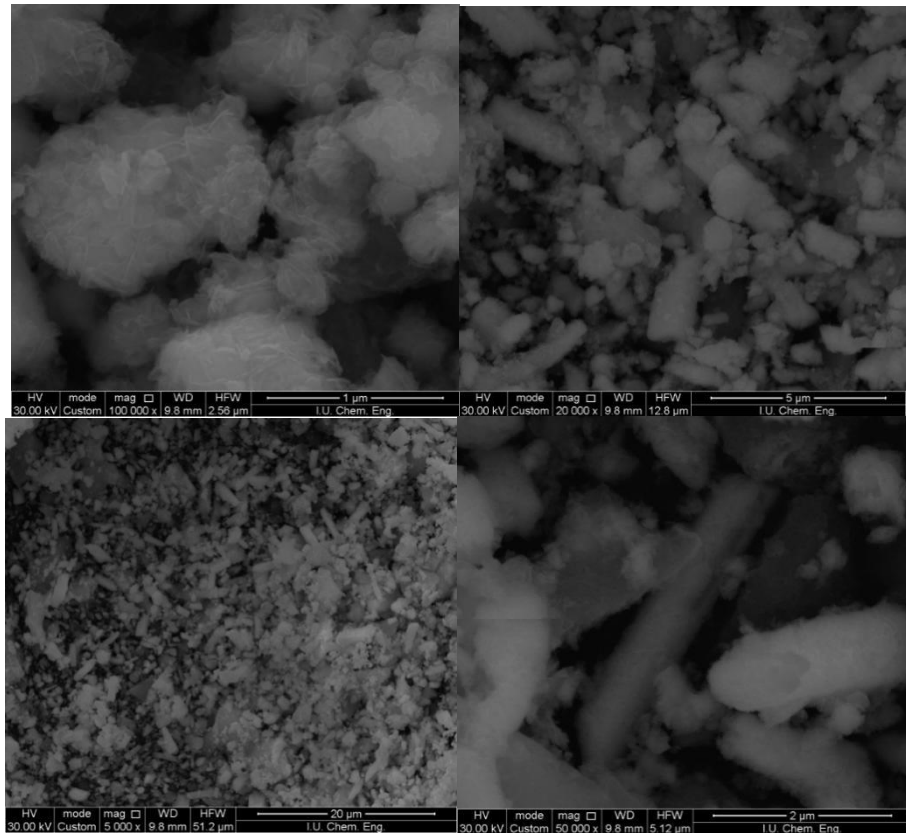**Figure 3.7:** SEM images of synthesized TiO_2-Bi_2O_3 binary oxide with different magnification.
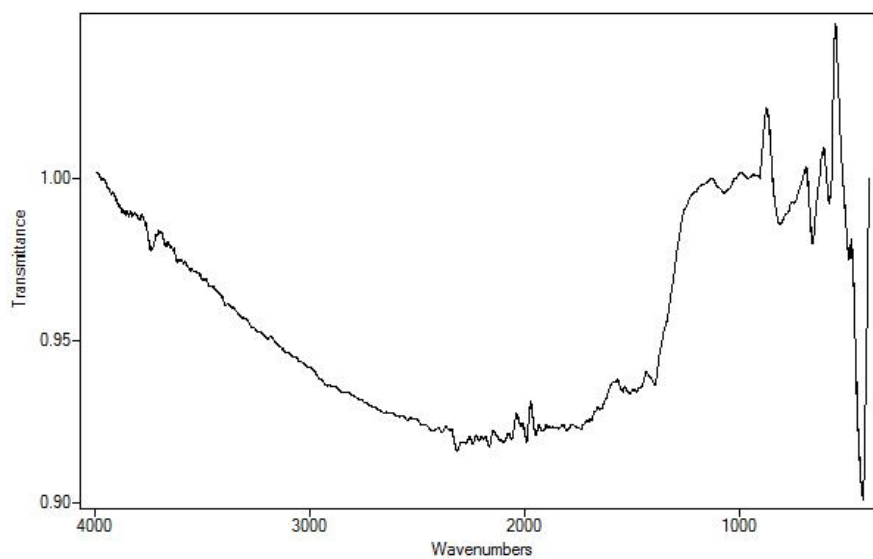
Figure 3.8: FT-IR spectrum of synthesized TiO_2-Bi_2O_3 binary oxide.

3.3 Characterization of ZnO-Bi₂O₃ Binary Oxide

Description of X-ray diffraction results for binary ZnO-Bi_2O_3 was presented in Figure 3.9, below. Peaks at 2θ values of 27.3 and 33.1 were the main peaks and used to calculate the crystallite size using the Debye-Scherer formula and the Bragg's law was used in calculating the spacing between planes. Figure 3.11 shows the spectrum result of prepared binary ZnO-Bi_2O_3.
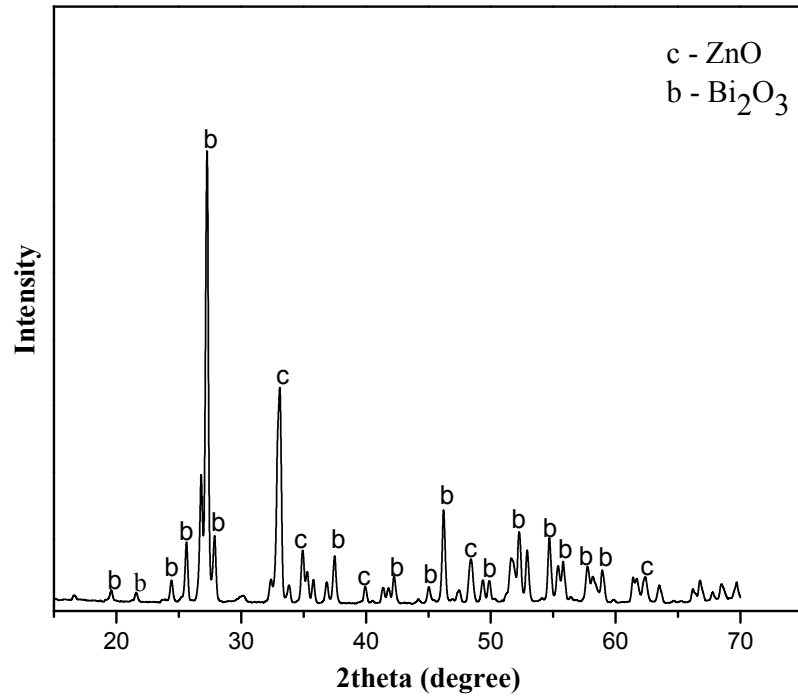
Figure 3.9: XRD pattern of as-synthesized ZnO-Bi_2O_3 binary oxide.
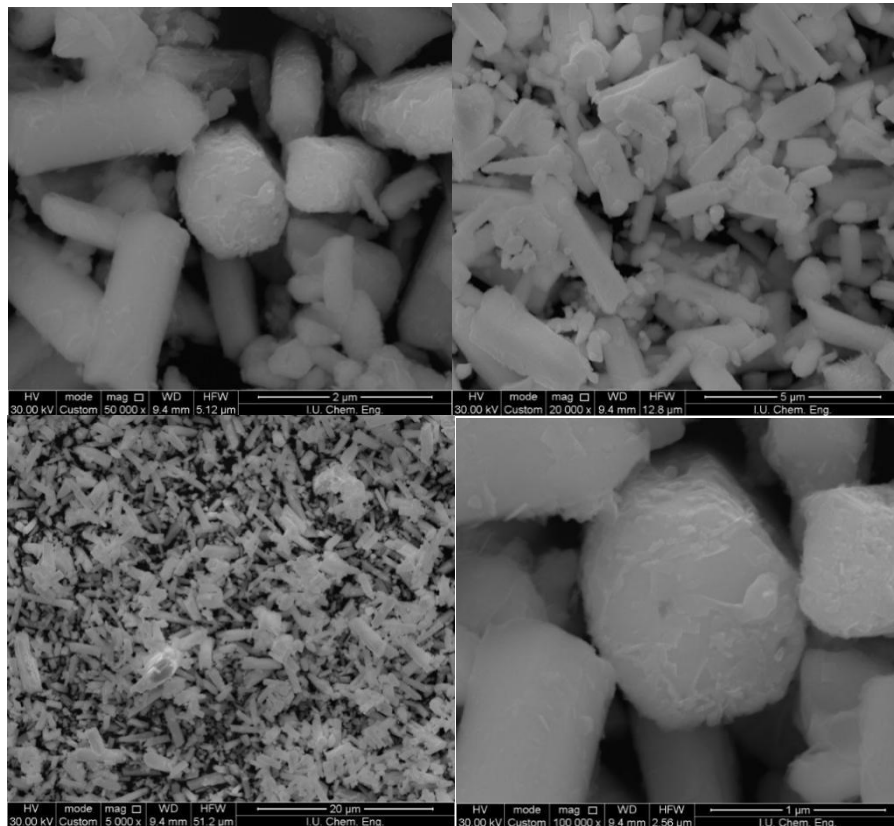
Figure 3.10: SEM images of as-synthesized ZnO-Bi_2O_3 binary oxide.
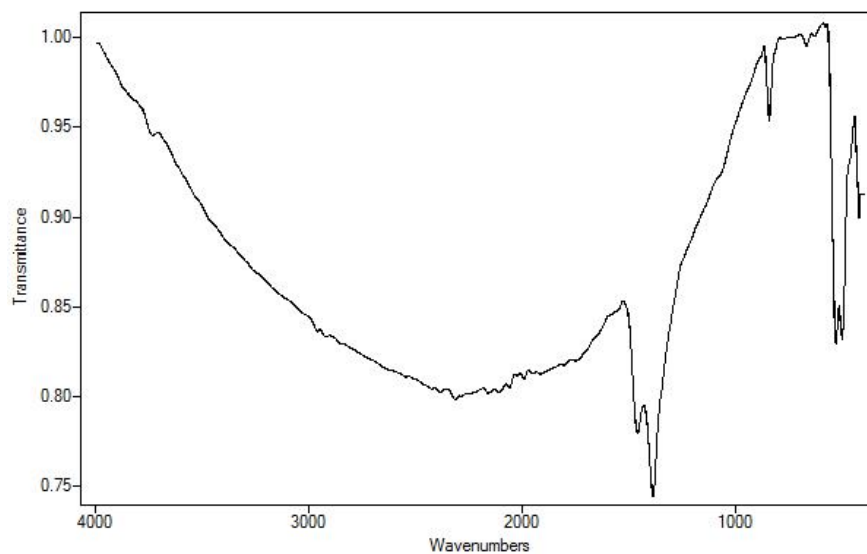
Figure 3.11: FT-IR spectrum of synthesized ZnO-Bi$_2$O$_3$ binary oxide

3.4 Characterization of ZrO$_2$-Bi$_2$O$_3$ Binary Oxide

Just like in the case of binary ZnO-Bi$_2$O$_3$, the illustration of the XRD patterns for ZrO$_2$-Bi$_2$O$_3$ binary oxide is given in Figure 3.12. Highest peaks at 2θ values were 27.1 and 30.0 and Bragg's equation was used in calculating the d values between planes.
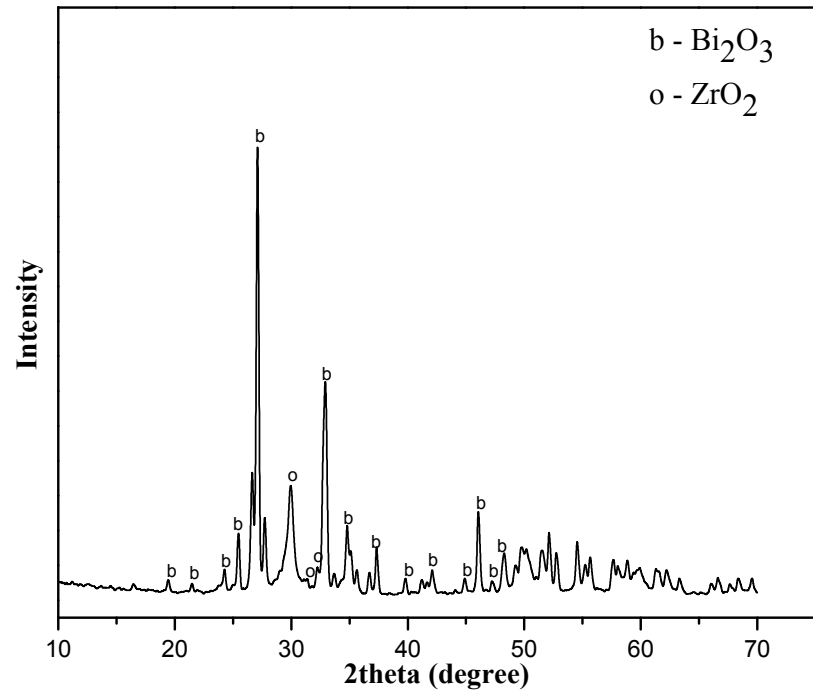
Figure 3.12: XRD pattern for as synthesized ZrO_2/Bi_2O_3 binary oxide.
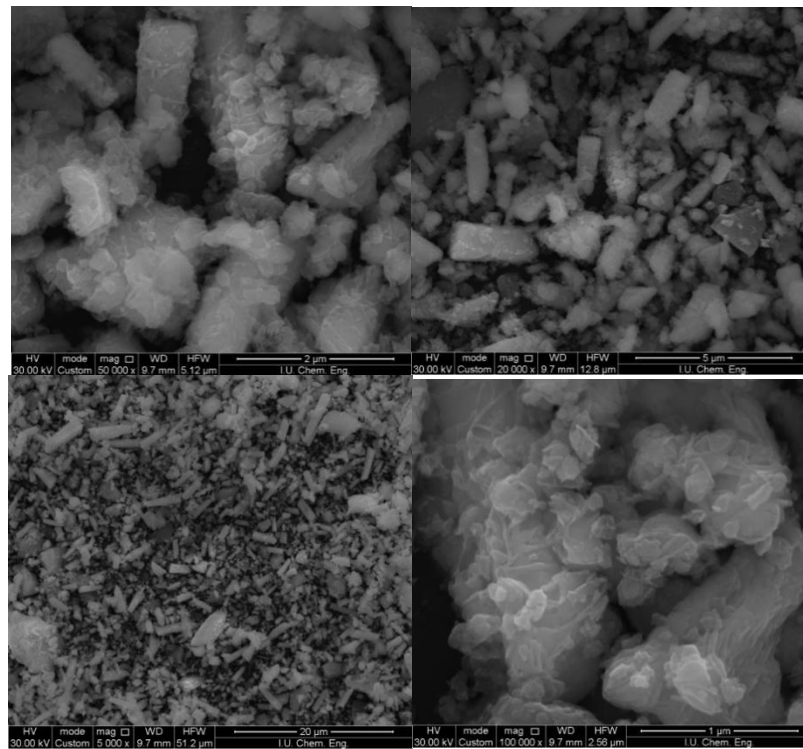
Figure 3.13: SEM images of as-synthesized ZrO_2-Bi_2O_3 binary oxide.
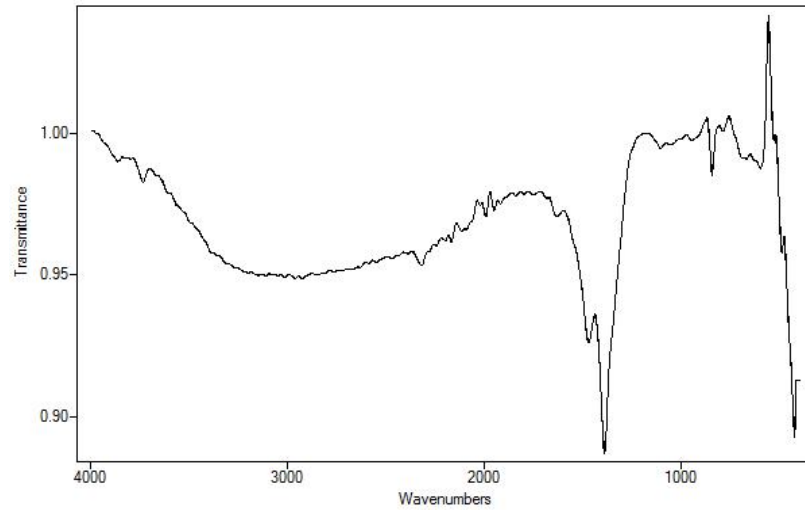
Figure 3.14: FT-IR spectrum of synthesized ZrO_2-Bi_2O_3 binary oxide.

3.5 Characterization of Bismuth Oxychloride Nanocomposite

Figure 3.15 illustrates the XRD pattern of synthesized bismuth oxychloride (BiOCl) nanocomposite. At 2θ value of 33.5 which was the most intensified peak (100% intensity) crystallite size of BiOCl using equation (2) was calculated and the spacing d, value was also calculated using Bragg's equation. In addition, Figure 3.16 shows the SEM morphologies of BiOCl product with different magnifications whereas, the result of the FT-IR analysis for BiOCl was presented in Figure 3.17.
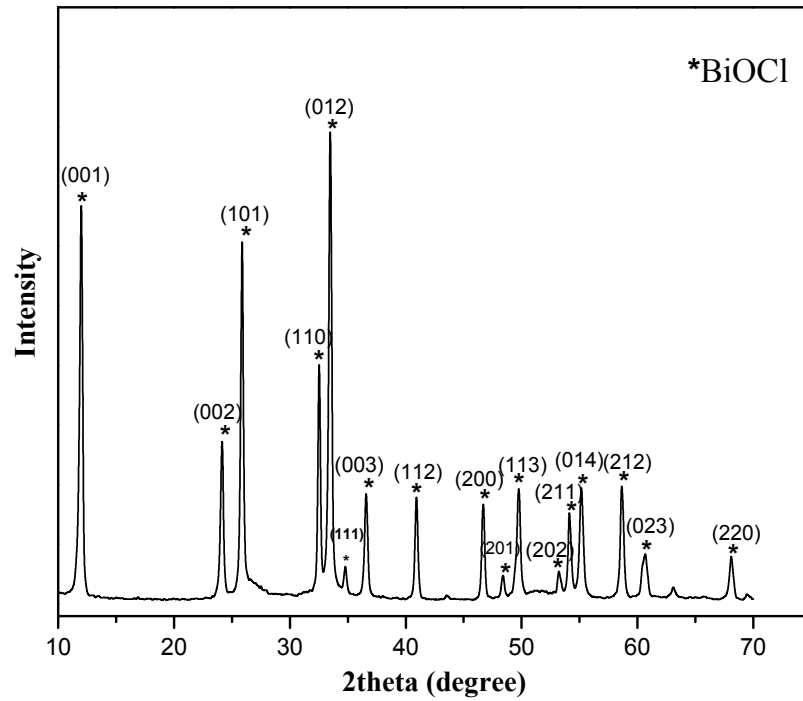
Figure 3.15: XRD pattern of as synthesized BiOCl.
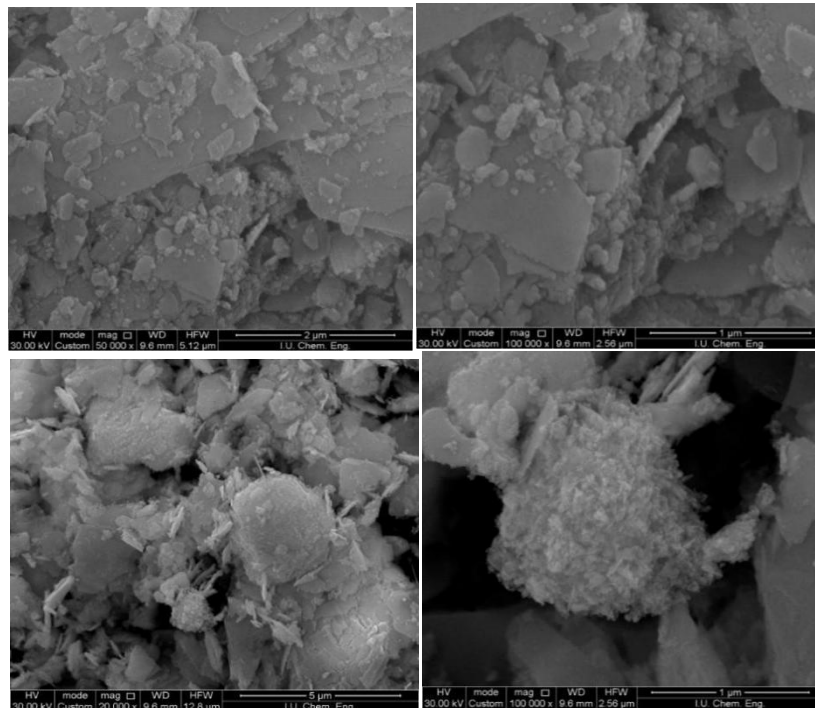
Figure 3.16: SEM images of synthesized BiOCl at different magnification.
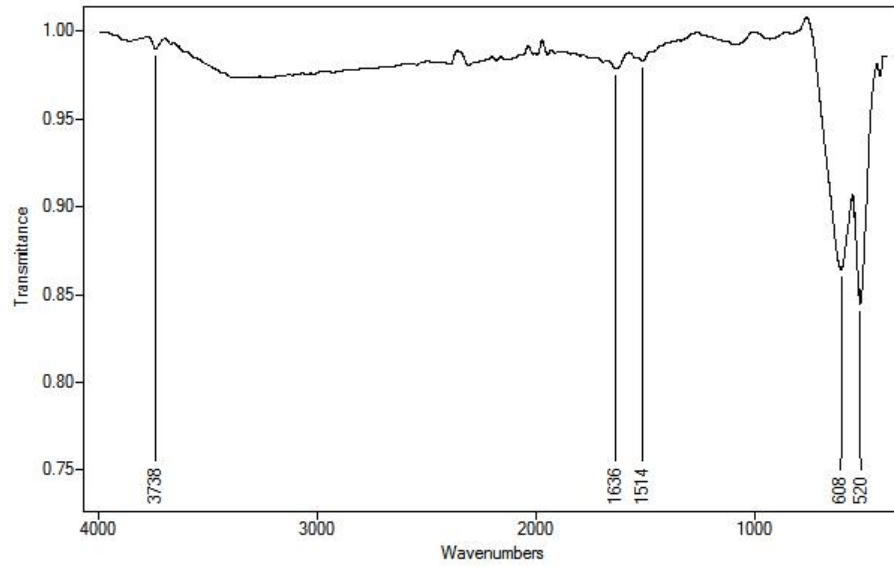
Figure 3.17: FT-IR spectrum of bismuth oxychloride.

4. DISCUSSION

4.1 Characterızatıon of SnO₂, TiO₂, Bi₂O₃, ZrO₂ and ZnO

From figure 3.1 intense peaks at 2θ values of 26.191, 33.586, 37.579, 51.405, 54.319, 57.864, 61.583, 64.497, 65.686 were in conformity with the work done by Sudha et al., 2012, in which observed peaks coincided with the results of bulk SnO₂ (ICDD 211250). The relative intensity and the position of the peak obviously established the existence of highly crystalline single tetragonal rutile phase of SnO_2 with JCPDS number #96-500-0225 and cell parameters a=4.7370 Å c=3.1850 Å.

Consequently, the crystalline dimension in the major plane (110) was calculated to be 12 nm. Width of the peaks was found to be 0.591, 0.687, 0.527, 0.667, 0.583, 0.756, 0.694, 0.800, and 0.738 (in nm) respectively for the prominent peaks, which also strongly suggests that particles were nano in size and the spacing between diffracting planes (d values) of SnO_2 sample calculated from Braggs equation ($2d.\sin\theta = n\lambda$) was put side by side with the d values of standard SnO_2 summarized by JCPDS 21-1250 and estimated the change in d was <1% (Table 3.1). Moreover, from figure 3.2 XRD peaks of all pure single synthesized oxides were found to be in agreement with previous researches and the crystalline sizes, morphologies and surface area presented in table 3.2.

The bismuth (III) oxide structures were morphologically nano rods whereas zinc oxide, titanium (IV) oxide and zirconium (IV) oxide were dark circular, white small circular with other non-circular and non-shaped white particles respectively from the SEM images. In the tin (IV) oxide SEM images, the nanoparticles have spherical morphologies. Dropping of ammonia to the solution slowly while stirring, high-speed diffusion of ammonia in the solution and reaction happening in a large area leads to the formation of many initial nucleases (Tazikeh *et al.*, 2014).

4.2 Characterization of TiO₂-Bi₂O₃ Binary Oxide

In figure 3.6, Bi₂O₃ appears to be presented more than TiO₂. The major 2θ values (peaks) for Bi₂O₃ and TiO₂ were 27.4 and 25.3 resulting to the diffraction patterns of (120) and (101) respectively, and were used in calculating (using equation 2) the crystallite size that was found to be 31 nm and 25.6 nm respectively, and thus,

confirming the presence of monoclinic α-Bi_2O_3 with JCPDS number #96-101-0005 and cell parameters a=5.8300 Å b=8.1400 Å c=7.4800 Å β=67.070º. Additionally, all the 2θ values were in consistence with monoclinic α-Bi_2O_3 preparation by (Oudghiri-Hassani *et al.*, 2015), and pure anatase phase of TiO_2 synthesis by (Bagheri *et al.*, 2013). Spacing between diffracting planes *(d)* were calculated using Bragg's equation and found to be 3.2534 Å and 3.5174 Å respectively of Bi_2O_3 and TiO_2.

Moreover, in all the three synthesized binary oxides seen from SEM figures, Bi_2O_3 has the white rod morphological structures with some thread like structures rap around it. In TiO_2-Bi_2O_3 binary oxide, the dark rod and circular structures represent the TiO_2, whereas dark small circular particles in ZnO-Bi_2O_3 binary oxide were ZnO structures and the small white particles attached to the Bi_2O_3 nanoparticles in ZrO_2-Bi_2O_3 binary oxide were ZrO_2 nano structures.

Prepared TiO_2-Bi_2O_3 binary oxide spectrum shows the absorption band at 664 cm^{-1} shows stretching vibration of Ti-O-Ti, also 493 cm^{-1} 428 cm^{-1} and 814 cm^{-1} as vibrations for Bi_2O_3 vibrations. Other bands observed are 1397 cm^{-1} and 586 cm^{-1} whereas 3738 cm^{-1} band indicate O–H vibration and presence of hydroxyl group and water molecule.

4.3 Characterization of ZnO-Bi_2O_3 Binary Oxide

Description of X-ray diffraction results for binary ZnO-Bi_2O_3 was presented in Figure 3.9. Peaks at 2θ values of 27.3 and 33.1 for monoclinic α-Bi_2O_3 with JCPDS number #96-101-0005 and cell parameters of a=5.8300 Å b=8.1400 Å c=7.4800 Å β=67.070º which was in relation with (Oudghiri-Hassani *et al.*, 2015) and ZnO with JCPDS file number #36-1451 respectively shows higher intensity than any other peak in the graph, and specifically, Bi_2O_3 has more intensity than ZnO. The crystallite sizes of both oxides were found to be 40 nm for Bi_2O_3 and 28.3 nm for ZnO with spacing between planes 3.2692 Å and 2.7074 Å for Bi_2O_3 and ZnO respectively.

Absorption bands in the FT-IR spectrum at 503 cm^{-1} and 422 cm^{-1} were vibrations of ZnO and 844 cm^{-1} for Bi_2O_3 vibration. 1460 cm^{-1}, 1389 cm^{-1}, 670 cm^{-1} and 533 cm^{-1} bands were also observed. Moreover, 3731 cm^{-1} band indicate O–H vibration and presence of hydroxyl group and water molecule.

4.4 Characterization of Binary ZrO_2-Bi_2O_3

Considering the XRD pattern in Figure 3.12 for binary ZnO-Bi_2O_3, peaks at 2θ values of 27.1 and 30.0 for monoclinic α-Bi_2O_3 with JCPDS file number #96-901-2547 having cell parameters a=5.8486 Å b=8.1661 Å c=7.5097 Å β=113.000º which was in agreement with (Communication *et al.*, 2015) and cubic phase ZrO_2 with ICDD #00-049-1642 (Reddy Channu *et al.*, 2011) resulting to the diffraction patterns of (120) and (101) respectively are the most intensified peaks of each oxide, and specifically, Bi_2O_3 has more intensity than ZrO_2. The crystallite sizes were found to be 42.5 nm Bi_2O_3 and 25.7 nm ZrO_2. The *d* values between planes were found to be 3.2876 Å and 2.9839 Å for Bi_2O_3 and ZrO_2 respectively.

FTIR results shows absorption bands at 490 cm^{-1} s due to ZrO_2 vibration mode, bands at 426 cm^{-1} and 844 cm^{-1} were for Bi_2O_3 vibration. Bands at 2319 cm^{-1} – 1632 cm^{-1}, 1472 cm^{-1}, 1391 cm^{-1} were assigned to C=O stretching, C–O stretching, C–C stretching and O–C=O in plane bending vibrations. Another bands observed were 601 cm^{-1}, 3732 cm^{-1} band indicate O–H vibration and presence of hydroxyl group and water molecule.

4.5 Characterization of Bismuth Oxychloride Nanocomposite

All peaks from the XRD data (figure 3.15) were confirmed to be representing a tetragonal phase of BiOCl intensity and was in agreement with (Ascencio-Aguirre *et al.*, 2017). Peak at 2θ value of 33.5 is the most intensified peak (100% intensity) and as such the calculated crystallite size of the BiOCl with JCPDS file number #96-900-8427 and cell parameters a=3.8870 Å c=7.3540 Å was found to be 37.6 nm. The spacing *d,* value of the main BiOCl peak was 2.6741 Å.

In the SEM analysis however, the product exhibits flat and circular sheet-shaped structure in some particles. Thus, there exist some smaller particles which could be other negligible oxides – likely SnO_2. The morphology of the BiOCl sheets is in relation and similar to the BiOCl sheets synthesized by (Li *et al.*, 2012).

Here, the FTIR spectrum of the BiOCl is in the 450-4000 cm^{-1} region. The weak bands showing in the range of 3200-3800 cm^{-1} with the absorption peak at 3738 cm^{-1} are assigned to the H–O–H stretching from water. The weak bands at 1636 cm^{-1} and 1514 cm^{-1} are due to adsorbed atmospheric CO_2 which results from the preparation and

processing of FTIR sample in the ambient atmosphere and the band at 608 cm^{-1} and 520 cm^{-1} are assigned to Bi–O bands (Li *et al.*, 2012).

However, table 4.1 summarizes the X-ray diffraction results, showing the highest intensity values used in calculations, crystalline size (D), spacing between diffracting planes (d value) and full width at half maximum of diffraction peak (β) used in calculations for all synthesized catalysts.

Table 4.1: Summary of XRD results for all synthesized catalysts

Catalyst	Highest Intensity at 2θ	Crystalline size (D) in nm	d value in Å
Binary TiO$_2$-Bi$_2$O$_3$	TiO$_2$ – 25.3	TiO$_2$ – 25.6	TiO$_2$ – 3.5174
	Bi$_2$O$_3$ – 27.4	Bi$_2$O$_3$ – 31	Bi$_2$O$_3$ – 3.2534
Binary ZnO-Bi$_2$O$_3$	ZnO – 33.1	ZnO – 28.3	ZnO – 2.7074
	Bi$_2$O$_3$ – 27.3	Bi$_2$O$_3$ – 40	Bi$_2$O$_3$ – 3.2692
Binary ZrO$_2$-Bi$_2$O$_3$	ZrO$_2$ – 30.0	ZrO$_2$ – 25.7	ZrO$_2$ – 2.9839
	Bi$_2$O$_3$ – 27.1	Bi$_2$O$_3$ – 42.5	Bi$_2$O$_3$ – 3.2876
Bismuth oxychloride nanocomposite	BiOCl – 33.5	BiOCl – 37.6	BiOCl – 2.6741

Catalysts	Crystallite size (nm)	S$_{BET}$ (m^{2}g^{-1})	Morphology
SnO$_2$	12	155	Tetragonal
α-Bi$_2$O$_3$	42	2	Monoclinic
TiO$_2$	43	40	Anatase
ZnO	65	28	Hexagonal
ZrO$_2$	7	96	Tetragonal

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

All pure single oxides (SnO_2, Bi_2O_3, TiO_2, ZnO and ZrO_2) synthesized by the sol-gel and co-precipitation methods were confirmed. The crystallites sizes were calculated, structure and morphologies and their various phases identified. The solid-state preparation of three binary oxides – basically ZrO_2-Bi_2O_3, ZnO-Bi_2O_3 and TiO_2-Bi_2O_3 – were confirmed and turned out to be in good agreement with previous studies. It was observed that there were changes in crystalline sizes of metallic oxides in binary oxide nanocomposites. In particular, in ZnO-Bi_2O_3 binary oxide, crystalline size of ZnO particle was rather reduced in comparison to pure ZnO particle. However, there occurred an increase of crystalline size of ZrO_2 particle in ZrO_2-Bi_2O_3 binary oxide, catalyst in comparison to pure ZrO_2 particle. Such changes occurring in crystalline sizes (grain size) indicate that metallic oxides (phases) are rather compatible with each other as result of solid state reactions. As result of substantial reactions on interfaces, new types of binary nano-composites were produced.

In the scope of this thesis study, due to the increase of ratios of atoms at boundaries and corners caused by such reductions occurred in grain sizes of the prepared binary oxides, it is obvious that these binary oxide mixtures will play an important role in catalytic reactions.

Moreover, in the XRD of the synthesized pure crystalline bismuth oxychloride nanocomposite, all peaks shows characteristic intensity for bismuth oxychloride and which was in good conformity with previous study (Ascencio-Aguirre *et al.*, 2017). Although there are some negligible particle sizes in the SEM images that could possibly be associated with SnO_2, the SEM images and the FT-IR bands just like XRD peaks also confirms the morphological structure and the bands respectively of BiOCl (Li *et al.*, 2012).

5.2 Recommendation

Thus, so far lots of pure oxides and quite a number of binary oxides have already been discovered, and into numerous applications. Viewing the fact that, photocatalysts play vital role in many aspects of catalysis ranging from chemical, energy, industrial, pharmaceuticals, water treatment, environmental remediation and many more, enhanced novel materials that will not only boost the significance of their role but also more commercially acceptable should be an area for researchers to explore. In other words, the development of multicomponent nanocomposite photocatalytic materials can never be over emphasized.

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APPENDICE I

$$2d.\sin\theta = n\lambda \text{ (Braggs equation) } ------------(1)$$

Where, d = spacing between diffracting planes

$$D = \frac{C\lambda}{\beta Cos\theta} \quad ------------------------------(2)$$

Where,

C = Constant usually with a value of 0.9 or 1

λ = X-ray wavelength of radiation used (Cu/K$_\alpha$= 1.54056 Å)

β = Full width at half maximum (FWHM) of diffraction peak

θ = Bragg diffraction angle

PARTICLE SIZE DETERMINATIONS

1. Pure SnO$_2$:

λ = 1.54056 Å

$\theta = \frac{26.191}{2} = 13.0955$

C = 1

β = 0.591 (to be converted into radian) » $\beta = 0.591 * \frac{3.14}{180} = 0.01031$R

inserting all values into equation 2:

» D = 120.7399957 Å = 12 nm

APPENDICES I (CONT.)

2. TiO₂-Bi₂O₃ Binary oxide

$\theta_{Bi2O3} = \frac{27.391}{2} = 13.6955$ and $\theta_{Bi2O3} = \frac{25.30}{2} = 12.65$

$\beta_{Bi2O3} = 0.289 * \frac{3.14}{180} = 0.005041444444R$ and $\beta_{TiO2} = 0.354 * \frac{3.14}{180} = 0.006175333333R$

inserting all values into equation 2:

» $D_{Bi2O3} = 31$ nm and $D_{TiO2} = 25.6$ nm

3. ZrO₂-Bi₂O₃ Binary oxide

$\theta_{Bi2O3} = \frac{27.101}{2} = 13.5505$ and $\theta_{ZrO2} = \frac{32.893}{2} = 16.4465$

$\beta_{Bi2O3} = 0.214 * \frac{3.14}{180} = 0.006245R$

» $D_{Bi2O3} = 42.45$ nm and $D_{ZrO2} = 25.7$ nm

4. ZnO-Bi₂O₃ Binary oxide

$\theta_{Bi2O3} = \frac{27.256}{2} = 13.628$

$\beta_{Bi2O3} = 0.226 * \frac{3.14}{180} = 0.00392444444R$

inserting all values into equation 2:

» $D_{Bi2O3} = 40$ nm and $D_{ZnO} = 28.3$ nm

5. BiOCl Nanocomposite

$\lambda = 1.54056$ Å, $\qquad\qquad\qquad\qquad\qquad$ $\beta = 0.245 * \frac{3.14}{180} = 0.00427389R$

$\theta = \frac{33.482}{2} = 16.741$ $\qquad\qquad\qquad\qquad\qquad$ inserting all values into equation 2:

$C = 1$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ » $D = 37.6$ nm

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